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## ( $\eta^5$ -Cyclopentadienyl){ $\eta^4$ -[1,3-bis(4-methoxyphenyl)-2,4-bis(trimethylsilyl)cyclobutadiene]}cobalt(I) (1) and ( $\eta^5$ -Cyclopentadienyl){ $\eta^4$ -[1,3-bis(trifluoromethylphenyl)-2,4-bis(trimethylsilyl)cyclobutadiene]}cobalt(I) (2)

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**Abstract.** (1)  $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{24}\text{H}_{32}\text{O}_2\text{Si}_2)]$ ,  $M_r = 532.65$ , monoclinic,  $P2_1/n$ ,  $a = 22.371$  (5),  $b = 9.170$  (4),  $c = 14.030$  (4) Å,  $\beta = 104.15$  (4)°,  $V = 2790.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.268$  g cm<sup>-3</sup>,  $\mu = 6.71$  cm<sup>-1</sup>,  $F(000) = 1104$ . (2)  $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{24}\text{H}_{26}\text{F}_6\text{Si}_2)]$ ,  $M_r = 608.67$ , monoclinic,  $P2_1/a$ ,  $a = 17.969$  (4),  $b = 14.056$  (4),  $c = 12.744$  (4) Å,  $\beta = 96.67$  (3)°,  $V = 3197.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.265$  g cm<sup>-3</sup>,  $\mu = 6.15$  cm<sup>-1</sup>,  $F(000) = 1376$  (2). Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $T = 295$  K,  $R = 0.037$  for 3188 (1) and 0.049 for 3955 (2) observed reflections. Although two types of substituents of very different electronic character are present in the phenyl rings of (1) and (2), no significant influence on the molecular structure within the coordination sphere is detected. In both compounds, the Co atom is half-way between the planes of the four- and five-membered coordinated rings. The cyclobutadiene ring is slightly contracted along the diagonal between the phenyl-substituted C atoms.

**Introduction.** In previous work (Brune & Horlbeck, 1973) the influence of substituents on the phenyl rings on the bonding properties and structures of tricarbonyl-(1,2-diphenylcyclobutadiene)iron(III) complexes were studied with NMR. The observation and interpretation

of different nuclear spin-spin coupling constants lead to the conclusion that significant modifications of the molecular geometry of the four-membered ring and its bonding to the central atom with change of electronic character of the substituents occur. To observe these changes directly, the crystal structure analysis was undertaken of both title compounds whose phenyl rings are substituted with a methoxy group in (1) as a strong  $\pi$ -donating substituent and the trifluoromethyl group in (2) as an efficient inductive  $\sigma$ -attracting one.

**Experimental.** Crystals of both title compounds are red-brown; (1) crystallizes in the form of elongated parallelepipeds, (2) in the form of octahedra, both with well developed faces. (1) Crystal  $0.2 \times 0.2 \times 0.4$  mm; (2) crystal  $0.2 \times 0.1 \times 0.3$  mm. 4914 (1) and 5643 (2) independent unique reflections; Philips PW 1100 four-circle diffractometer; Mo  $K\alpha$  radiation, graphite monochromator;  $\theta$ - $2\theta$  scan, 3188 observed reflections for (1) [ $F > 1.5\sigma(F)$ ,  $-26 \leq h \leq 25$ ,  $0 \leq k \leq 10$ ,  $0 \leq l \leq 16$ ,  $\theta_{\min} = 2$ ,  $\theta_{\max} = 25^\circ$ ] and 3955 observed reflections for (2) [ $F > 1.5\sigma(F)$ ,  $-21 \leq h \leq 21$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 15$ ,  $\theta_{\min} = 2$ ,  $\theta_{\max} = 25^\circ$ ]. The intensity of three standards did not vary during the period of measurement. The cell parameters were

obtained from the refinement of 25 reflections [ $7 < \theta < 19^\circ$  for (1) and  $8 < \theta < 16^\circ$  for (2)]. No absorption correction. Both structures were determined with direct methods using the random-phase approach (Debaerdemaeker & Woolfson, 1983) and the XMY84 program (Debaerdemaeker, 1984). In each case the best combined figure of merit showed most of the structure. The structure was refined by full-matrix least squares on  $F$ , first with isotropic and then with anisotropic temperature parameters, using unit weights (Sheldrick, 1977), until the parameter shifts were less than the corresponding standard deviation. The H atoms were found from difference Fourier maps. The introduction and refinement of all the H atoms with isotropic temperature factors led to  $R$  values of 0.037 (1) and 0.049 (2) but some of the H-atom temperature factors look unrealistic.  $wR = 0.037$  (1), 0.049 (2),  $w = 1$ . Max.  $\Delta/\sigma = 0.09$  (1), 0.08 (2). Max. peak in final difference map  $0.3 \text{ e } \text{\AA}^{-3}$  for (1) and  $1.2 \text{ e } \text{\AA}^{-3}$  (2), average  $0.02 \text{ e } \text{\AA}^{-3}$  (1),  $0.43 \text{ e } \text{\AA}^{-3}$  (2). Scattering factors of Cromer & Mann (1968) and Doyle & Turner (1968).\*

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, main interatomic distances and angles in Tables 2 and 3. Figs. 1 and 2 show the structure of a single molecule of (1) and (2) in the same orientation with the atomic numbering (Motherwell, 1978).

Although two types of substituents of very different electronic character have been introduced into the phenyl rings, the basic structures of (1) and (2) coincide to a high degree. This similarity exists also with the — although only partially determined — structure data of the unsubstituted parent compound [Co( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^4$ -{1,3-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-2,4-[(CH<sub>3</sub>)<sub>2</sub>Si]<sub>2</sub>C<sub>4</sub>)] (3). In (1) and (2) the Co atom is situated nearly exactly centrally between the planes of the four- and five-membered rings, which are practically parallel. The cyclobutadiene is somewhat contracted in the diagonal direction between the two phenyl-substituted C atoms. The angles in the four-membered ring at C(20) and C(40) are  $92^\circ$ , those at C(10) and C(30), as a consequence of the substitution with trimethylsilyl groups,  $88^\circ$ . This difference is obviously caused by the difference in electronegativity values between Si (2.1) and C( $sp^2$ ) (2.8) (Bent, 1961) of the phenyl rings. According to Bent's (1961) principle, the bonding of the lower electronegative Si at C(10) and C(30) causes an enhancement of  $s$  character in those hybrid orbitals of C(10) and C(30) that are used for Si—C bonding. As a consequence, there is an

increase of  $p$  character in those orbitals of C(10) and C(30) by which the C—C  $\sigma$  bonds of the four-membered ring are built up; as a consequence of this

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Compound (1)	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C(1)	0.7165 (2)	0.2860 (6)	0.3860 (5)	0.098 (7)
C(10)	0.5951 (1)	0.1070 (3)	0.4243 (2)	0.035 (2)
C(11)	0.5861 (2)	0.4213 (4)	0.4899 (3)	0.067 (4)
C(12)	0.5381 (2)	0.1742 (6)	0.5946 (3)	0.083 (6)
C(13)	0.6765 (2)	0.2162 (5)	0.6205 (3)	0.078 (5)
C(2)	0.7462 (1)	0.1553 (6)	0.3782 (4)	0.088 (6)
C(20)	0.6213 (1)	−0.0322 (3)	0.4034 (2)	0.035 (3)
C(21)	0.6602 (1)	−0.1421 (3)	0.4649 (2)	0.036 (3)
C(22)	0.6585 (1)	−0.1635 (4)	0.5623 (2)	0.048 (3)
C(23)	0.6959 (1)	−0.2649 (4)	0.6208 (2)	0.053 (4)
C(24)	0.7356 (1)	−0.3487 (4)	0.5834 (2)	0.044 (3)
C(24')	0.8212 (2)	−0.5130 (5)	0.6226 (3)	0.075 (5)
C(25)	0.7379 (1)	−0.3311 (3)	0.4877 (2)	0.043 (3)
C(26)	0.7010 (1)	−0.2275 (3)	0.4295 (2)	0.041 (3)
C(3)	0.7280 (2)	0.1139 (5)	0.2807 (4)	0.079 (5)
C(30)	0.5890 (1)	−0.0251 (3)	0.2993 (2)	0.036 (3)
C(31)	0.5826 (2)	−0.3430 (5)	0.2344 (4)	0.099 (6)
C(32)	0.6148 (2)	−0.1086 (6)	0.1001 (3)	0.090 (6)
C(33)	0.4865 (1)	−0.1319 (5)	0.1315 (3)	0.066 (4)
C(4)	0.6888 (2)	0.2169 (7)	0.2299 (3)	0.085 (6)
C(40)	0.5628 (1)	0.1150 (3)	0.3205 (2)	0.037 (3)
C(41)	0.5164 (1)	0.2131 (3)	0.2614 (2)	0.038 (3)
C(42)	0.5164 (1)	0.2481 (4)	0.1660 (2)	0.053 (4)
C(43)	0.4723 (2)	0.3405 (4)	0.1106 (2)	0.062 (4)
C(44)	0.4270 (1)	0.3967 (4)	0.1504 (3)	0.063 (4)
C(44')	0.3385 (2)	0.5480 (7)	0.1288 (5)	0.129 (8)
C(45)	0.4262 (1)	0.3650 (4)	0.2447 (3)	0.061 (4)
C(46)	0.4708 (1)	0.2720 (4)	0.2992 (2)	0.051 (3)
C(5)	0.6820 (2)	0.3231 (5)	0.2941 (6)	0.096 (7)
Co(1)	0.6527 (1)	0.1290 (1)	0.3369 (1)	0.037 (1)
O(24)	0.7704 (1)	−0.4470 (3)	0.6475 (2)	0.066 (3)
O(44)	0.3852 (1)	0.4859 (3)	0.0891 (2)	0.097 (4)
Si(10)	0.5991 (1)	0.2283 (1)	0.5320 (1)	0.046 (1)
Si(30)	0.5696 (1)	−0.1520 (1)	0.1922 (1)	0.046 (1)
Compound (2)				
C(1)	0.5754 (4)	0.1721 (6)	0.0531 (5)	0.063 (8)
C(10)	0.7076 (3)	0.0598 (4)	0.2240 (4)	0.039 (5)
C(11)	0.6654 (5)	−0.1223 (6)	0.3301 (6)	0.078 (10)
C(12)	0.7587 (5)	−0.1315 (6)	0.1505 (7)	0.084 (10)
C(13)	0.5954 (4)	−0.0839 (6)	0.1086 (6)	0.075 (9)
C(2)	0.6181 (4)	0.2503 (6)	0.0413 (6)	0.063 (8)
C(20)	0.7582 (3)	0.1242 (4)	0.1760 (4)	0.040 (5)
C(21)	0.8014 (3)	0.1157 (4)	0.0868 (4)	0.040 (5)
C(22)	0.7697 (3)	0.0864 (5)	−0.0118 (5)	0.054 (7)
C(23)	0.8108 (4)	0.0801 (5)	−0.0959 (5)	0.057 (7)
C(24)	0.8855 (4)	0.1025 (5)	−0.0824 (5)	0.052 (7)
C(240)	0.9298 (5)	0.0981 (6)	−0.1732 (7)	0.074 (10)
C(25)	0.9180 (4)	0.1309 (6)	0.0138 (6)	0.069 (9)
C(26)	0.8771 (3)	0.1370 (6)	0.0988 (5)	0.060 (7)
C(3)	0.6150 (4)	0.3084 (5)	0.2268 (6)	0.067 (8)
C(30)	0.7586 (3)	0.1926 (4)	0.2619 (4)	0.039 (5)
C(31)	0.8210 (4)	0.3655 (6)	0.1656 (6)	0.072 (9)
C(32)	0.8930 (4)	0.2967 (7)	0.3767 (6)	0.080 (10)
C(33)	0.7414 (5)	0.3864 (6)	0.3621 (6)	0.075 (9)
C(4)	0.5694 (4)	0.2662 (6)	0.1929 (6)	0.072 (9)
C(40)	0.7075 (3)	0.1292 (4)	0.3099 (4)	0.038 (5)
C(41)	0.6776 (3)	0.1295 (4)	0.4110 (4)	0.039 (5)
C(42)	0.7205 (3)	0.1585 (5)	0.5017 (5)	0.050 (6)
C(43)	0.6932 (3)	0.1595 (5)	0.5986 (5)	0.056 (7)
C(44)	0.6212 (3)	0.1305 (5)	0.6049 (4)	0.048 (6)
C(440)	0.5890 (4)	0.1316 (6)	0.7072 (6)	0.071 (9)
C(45)	0.5769 (3)	0.0998 (5)	0.5164 (5)	0.055 (7)
C(46)	0.6057 (3)	0.0991 (5)	0.4201 (5)	0.053 (7)
C(5)	0.5449 (3)	0.1808 (6)	0.1479 (6)	0.069 (8)
Co(1)	0.6584 (1)	0.1803 (1)	0.1769 (1)	0.040 (1)
F(241)	0.9433 (5)	0.0136 (5)	−0.2014 (7)	0.146 (13)
F(242)	0.8931 (6)	0.1353 (9)	−0.2600 (6)	0.179 (18)
F(243)	0.9912 (5)	0.1451 (8)	−0.1612 (7)	0.174 (16)
F(441)	0.5515 (3)	0.0494 (5)	0.7216 (5)	0.093 (8)
F(442)	0.6403 (3)	0.1364 (6)	0.7891 (4)	0.108 (10)
F(443)	0.5401 (4)	0.1966 (5)	0.7130 (5)	0.120 (10)
Si(10)	0.6806 (1)	−0.0673 (1)	0.2029 (1)	0.049 (1)
Si(30)	0.8025 (1)	0.3095 (1)	0.2916 (1)	0.050 (1)

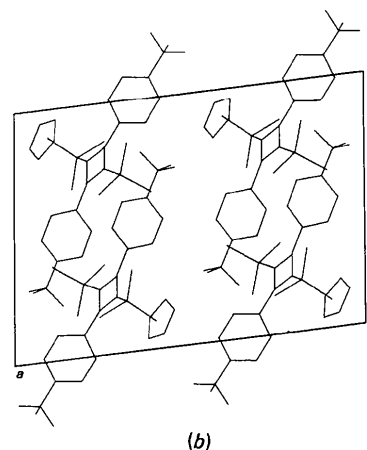
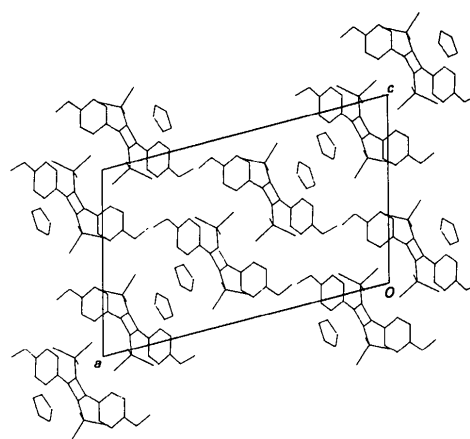
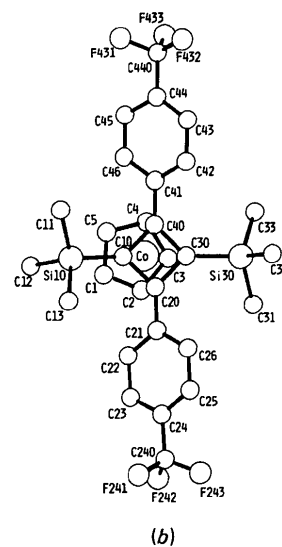
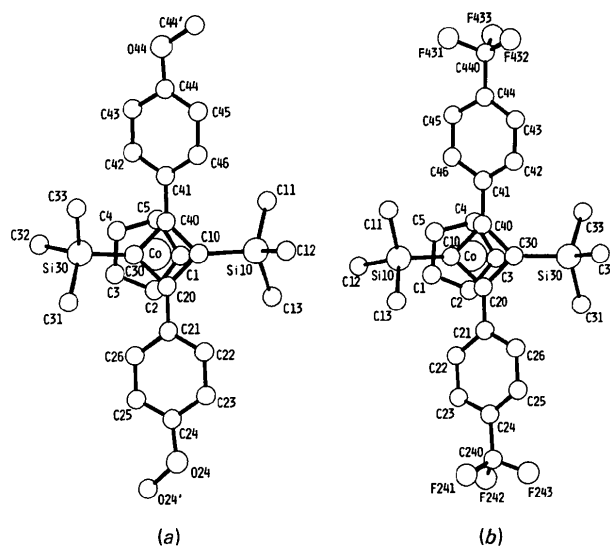
\* Lists of structure factors, anisotropic thermal parameters, all bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43359 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Main interatomic distances (Å) with e.s.d.'s in parentheses

	(1)	(2)		(1)	(2)
Co(1)—C(1)	2.025(5)	2.045(6)	C(30)—Si(30)	1.865(3)	1.843(8)
Co(1)—C(2)	2.042(5)	2.047(6)	Si(30)—C(31)	1.848(5)	1.853(9)
Co(1)—C(3)	2.032(6)	2.036(7)	Si(30)—C(32)	1.868(5)	1.856(8)
Co(1)—C(4)	2.036(6)	2.032(6)	Si(30)—C(33)	1.857(4)	1.847(9)
Co(1)—C(5)	2.037(5)	2.029(6)	C(40)—C(41)	1.467(4)	1.454(9)
Co(1)—C(10)	1.995(4)	1.972(6)	C(4) $ n$ —C(4) $ n+1$	1.376(6)	1.377(9)
Co(1)—C(20)	1.967(3)	1.961(6)	C(44)—O(44)	1.374(5)	—
Co(1)—C(30)	1.984(3)	1.999(5)	O(44)—C(44')	1.417(8)	—
Co(1)—C(40)	1.971(3)	1.954(6)	C(44)—C(440)	—	1.486(11)
C(1)—C(2)	1.388(8)	1.359(12)	C(10)—C(20)	1.463(5)	1.466(9)
C(1)—C(5)	1.374(10)	1.389(11)	C(10)—C(40)	1.462(4)	1.467(9)
C(2)—C(3)	1.381(7)	1.368(12)	C(20)—C(30)	1.464(4)	1.457(9)
C(3)—C(4)	1.366(8)	1.375(12)	C(30)—C(40)	1.472(5)	1.462(9)
C(4)—C(5)	1.360(10)	1.381(13)	C(240)—F(241)	—	1.273(12)
C(10)—Si(10)	1.861(4)	1.861(7)	C(240)—F(242)	—	1.327(13)
Si(10)—C(11)	1.866(4)	1.845(9)	C(240)—F(243)	—	1.281(14)
Si(10)—C(12)	1.863(6)	1.848(8)	C(440)—F(441)	—	1.362(12)
Si(10)—C(13)	1.870(4)	1.856(10)	C(440)—F(432)	—	1.310(9)
C(20)—C(21)	1.467(4)	1.454(9)	C(440)—F(433)	—	1.276(12)
C(2) $ n$ —C(2) $ n+1$	1.379(5)	1.374(10)			
C(24)—O(24)	1.373(4)	—			
O(24)—C(24')	1.406(6)	—			
C(24)—C(240)	—	1.479(12)			

Table 3. Main interatomic angles (°) with e.s.d.'s in parentheses

	(1)	(2)
C(2)—C(1)—C(5)	108.0(6)	108.0(8)
C(1)—C(2)—C(3)	106.5(6)	108.6(7)
C(2)—C(3)—C(4)	108.9(5)	108.3(7)
C(3)—C(4)—C(5)	108.1(6)	107.7(7)
C(1)—C(5)—C(4)	108.5(5)	107.4(8)
C(20)—C(10)—C(40)	88.2(3)	87.4(5)
C(10)—C(20)—C(30)	92.1(2)	92.5(5)
C(20)—C(30)—C(40)	87.8(3)	87.9(5)
C(10)—C(40)—C(30)	91.9(2)	92.2(5)
Si(10)—C(10)—C(20)	137.9(2)	134.1(5)
Si(10)—C(10)—C(40)	133.9(2)	136.4(5)
C(10)—C(20)—C(21)	133.6(3)	133.5(6)
C(21)—C(20)—C(30)	134.0(3)	133.3(6)
C(20)—C(30)—Si(30)	137.4(3)	135.0(6)
Si(30)—C(30)—C(40)	133.0(2)	137.0(5)
C(10)—C(40)—C(41)	134.6(3)	134.1(6)
C(30)—C(40)—C(41)	133.1(3)	133.2(5)
C(10)—Si(10)—C(11)	109.7(2)	109.8(3)
C(10)—Si(10)—C(12)	109.2(2)	108.9(4)
C(10)—Si(10)—C(13)	110.9(2)	113.4(3)
C(11)—Si(10)—C(12)	109.0(2)	107.9(4)
C(11)—Si(10)—C(13)	108.3(2)	108.8(4)
C(12)—Si(10)—C(13)	109.7(2)	107.9(4)
C(30)—Si(30)—C(31)	110.3(2)	108.5(5)
C(30)—Si(30)—C(32)	111.4(2)	111.0(6)
C(30)—Si(30)—C(33)	108.5(2)	110.9(6)
C(31)—Si(30)—C(32)	110.7(3)	108.3(5)
C(31)—Si(30)—C(33)	107.6(2)	110.5(7)
C(32)—Si(30)—C(33)	108.2(2)	107.6(6)
C(20)—C(21)—C(22)	121.4(3)	122.3(5)
C(20)—C(21)—C(26)	121.8(3)	120.2(6)
C(2) $ n$ —C(2) $ n+1$ —C(2) $ n+2$	120.0(4)	120.0(6)
C(23)—C(24)—O(24)	115.7(3)	—
C(25)—C(24)—O(24)	124.7(4)	—
C(24)—O(24)—C(24')	118.9(3)	—
C(23)—C(24)—C(240)	—	120.0(7)
C(25)—C(24)—C(240)	—	120.3(7)
C(24)—C(240)—F(241)	—	113.4(9)
C(24)—C(240)—F(242)	—	112.1(9)
C(24)—C(240)—F(243)	—	114.9(8)
C(40)—C(41)—C(42)	121.6(3)	121.1(6)
C(40)—C(41)—C(46)	121.0(3)	121.4(5)
C(4) $ n$ —C(4) $ n+1$ —C(4) $ n+2$	120.0(4)	120.0(6)
C(43)—C(44)—O(44)	115.2(4)	—
C(45)—C(44)—O(44)	124.6(4)	—
C(44)—O(44)—C(44')	116.6(4)	—
C(43)—C(44)—C(440)	—	120.9(6)
C(45)—C(44)—C(440)	—	118.5(6)
C(44)—C(440)—F(441)	—	111.0(7)
C(44)—C(440)—F(442)	—	113.0(7)
C(44)—C(440)—F(443)	—	113.5(7)

Fig. 1. Projection of compounds in the *ac* plane. (a) Compound (1); (b) compound (2).Fig. 2. Parallel projection along the *b* axis of both compounds. (a) Compound (1); (b) compound (2).

alteration in  $p$  character the C—C—C angles at C(10) and C(30) decrease and increase at C(20) and C(40). The mean values of the C—C bond lengths in the cyclobutadiene moiety are 1.465 in (1), 1.463 in (2) and 1.467 Å in the unsubstituted parent compound (3); with reference to these – within experimental error – no influence of the substituents on bond lengths is detectable. (1) and (2) are characterized by two more common structural features.

The three *exo* bonds of the cyclobutadiene, C(20)—C(21), C(40)—C(41) and C(30)—Si(30), are distorted out of the plane of the four-membered ring in the direction opposite to the Co atom [C(21): 0.088 (5), C(41): 0.12 (5), Si(30): 0.333 (6) Å for (1) and 0.154 (6), 0.130 (6), 0.371 (7) Å for (2)], while C(10)—Si(10) is in this plane [Si(10): -0.010 (5) for (1) and -0.030 (7) Å for (2)]. This difference between the positions of Si(10) and Si(20), relative to the cyclobutadiene plane, is probably caused by the different environment of the two atoms in the unit cell and shows an external influence on the molecular structure by packing effects.

Two of the three methyl groups of both trimethylsilyl substituents are orientated in directions such that

their steric interference with the two – with respect to the cyclobutadiene plane – distorted phenyl rings is a minimum. The only significant differences in the structures of (1) and (2) are the angles between the planes of the phenyl rings and cyclobutadiene: they are 40.5 (3) and 32.5 (4)° in (1), lower than 45.2 (5) and 41.6 (5)° found in (2).

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## Structure of [N(CH<sub>3</sub>)<sub>4</sub>][VOF<sub>3</sub>(H<sub>2</sub>O)]

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**Abstract.** Tetramethylammonium aquatetrafluorooxovanadate(IV), [N(CH<sub>3</sub>)<sub>4</sub>][VOF<sub>3</sub>(H<sub>2</sub>O)],  $M_r = 216.1$ , triclinic,  $P\bar{1}$ ,  $a = 7.000$  (3),  $b = 8.120$  (4),  $c = 9.050$  (4) Å,  $\alpha = 65.85$  (2),  $\beta = 83.08$  (3),  $\gamma = 72.97$  (3)°,  $V = 448.8$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 222$ ,  $D_x = 1.59$ ,  $D_m = 1.60$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 10.4$  mm<sup>-1</sup>, room temperature,  $R = 4.7\%$  for 1638 independent reflections. The vanadyl ion VO<sup>2+</sup> [V—O bond distance 1.598 (3) Å] is coordinated to four fluorine atoms and to one H<sub>2</sub>O molecule occupying a *cis* position relative to the vanadyl oxygen. These octahedra share one F—F edge forming discrete [V<sub>2</sub>O<sub>2</sub>F<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> dimers that are connected by hydrogen bonds.

**Introduction.** The investigation of the system CsF—VO<sub>2</sub>—HF (aq.) showed the existence of compounds in which V atoms constitute discrete units or isolated chains (Waltersson, 1978, 1979*a,b*). Up to now no

crystallographic investigation has been made on systems in which CsF is replaced by tetramethylammonium fluoride. The aim of this study was therefore to prepare corresponding compounds, the substitution of Cs<sup>+</sup> ions by N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ions being supposed to favour formation of magnetic entities or isolated magnetic chains.

The starting materials were tetramethylammonium fluoride tetrahydrate, [N(CH<sub>3</sub>)<sub>4</sub>]F.4H<sub>2</sub>O (p.a. Fluka), V<sub>2</sub>O<sub>5</sub> (p.a. Merck) and V<sub>2</sub>O<sub>3</sub> obtained by reduction of V<sub>2</sub>O<sub>5</sub> with hydrogen. A 1:1 (molar) mixture of V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>3</sub> was first dissolved in a 40% HF solution. The fluoride was added to the solution in the ratio N(CH<sub>3</sub>)<sub>4</sub>/V = 1. Upon evaporating the solution at room temperature blue crystals are obtained which are characteristic of V<sup>IV</sup>.

**Experimental.** Precession and Weissenberg photographs: triclinic Enraf—Nonius CAD-3 diffractometer with Mo  $K\alpha$  radiation. Crystal size 0.25 × 0.2 × 0.15 mm. Unit