

The exocyclic carbon (C) is bent toward Fe and away from Cr, with angles of 0.89 and -0.64° respectively, the angle is defined as the angle between the exocyclic C—C bond and the Cp ring with positive angle toward metal. The carbonyl plane [C(11), C, O, C(21)] is turned away from the corresponding ring Cp<sup>1</sup>(Fe) and Cp(Cr) by 14.7 and 14.3°, respectively. These rotations might be the result of intramolecular steric interference between atoms H[C(15)] and H[C(25)]. This is supported by the enlargement of bond angles C(15)—C(11)—C and C(25)—C(21)—C to 130.6 (3) and 132.5 (3)°, respectively.

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## Bis(arene)vanadium Complexes. A Structural Study

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**Abstract.** Bis(η<sup>6</sup>-mesitylene)vanadium(0), (1): [V(C<sub>9</sub>H<sub>12</sub>)<sub>2</sub>], *M<sub>r</sub>* = 291.3, orthorhombic, *Ccca*, *a* = 19.529 (1), *b* = 29.559 (2), *c* = 16.446 (4) Å, *V* = 9493 (3) Å<sup>3</sup>, *Z* = 24, *D<sub>x</sub>* = 1.23 g cm<sup>-3</sup>, graphite-monochromated Mo *Kα* radiation, λ = 0.71069 Å, μ = 5.64 cm<sup>-1</sup>, *F*(000) = 3720, *T* = 293 K, *R* = 0.058 for 1522 independent reflections. Potassium bis(η<sup>6</sup>-mesitylene)vanadate dioxane/tetrahydrofuran (0.5/1) solvate, (2): K[V(C<sub>9</sub>H<sub>12</sub>)<sub>2</sub>].C<sub>4</sub>H<sub>8</sub>O.½C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, monoclinic, *P2<sub>1</sub>/n* (the space group assignment was not unambiguous), *a* = 10.213 (2), *b* = 18.518 (3), *c* = 13.402 (3) Å, β = 89.58 (1)°, *V* = 2535 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.17 g cm<sup>-3</sup>, Mo *Kα* radiation, λ = 0.71069 Å, μ = 5.56 cm<sup>-1</sup>, *F*(000) = 952, *T* = 293 K, *R* = 0.073 for 1211 independent reflections. The asymmetric unit of (1) contains one eclipsed sandwich molecule in a general position and half a molecule lying around a crystallographic *C*<sub>2</sub> axis. The

ionic species (2) retains the sandwich structure and establishes contact ion pairs with the K<sup>+</sup> cations, which also interact with tetrahydrofuran and dioxane solvent molecules in a complex packing pattern.

**Introduction.** Despite the richness of the organometallic chemistry of Group V elements, the structural data available in the literature on bis(arene) complexes of vanadium are very scarce (Fischer, Fritz, Manchot, Priebe & Schneider, 1963; Radonovich, Zuerner, Efner & Klabunde, 1976). Bis(arene)vanadium anions are extremely air sensitive and require great care in both their synthesis and solid-state characterization. In a preliminary report (Fochi, Braga & Sabatino, 1988) we showed that reduction of bis(arene)vanadium(0) complexes with potassium in coordinating ethereal solvents gives solutions of the corresponding bis(arene)vanadium(-1) derivatives (arene = benzene, mesitylene). Solvated potassium salts were isolated in yields depending on the

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Table 1. *Experimental data for (1) and (2)*

|   | (1)                                  | (2)                    |
|---|--------------------------------------|------------------------|
| No. of reflections for lattice parameters                     | 25                                   | 25                     |
| $\theta$ range ( $^\circ$ )                                   | 8–13                                 | 7–16                   |
| Diffractometer  | Nonius CAD-4                         | Nonius CAD-4           |
| Black-brown crystal, size (mm)                                | 0.1 × 0.2 × 0.2                      | 0.2 × 0.2 × 0.4        |
| Scan range ( $^\circ$ )                                       | 2.5 < $\theta$ < 25                  | 2.5 < $\theta$ < 25    |
| Scan type   | $\omega/2\theta$                     | $\omega/2\theta$       |
| Scan interval ( $^\circ$ )                                    | 0.8 + 0.35tan $\theta$               | 0.7 + 0.35tan $\theta$ |
| Prescan speed ( $^\circ$ min $^{-1}$ )                        | 5                                    | 6                      |
| Prescan acceptance $\sigma(I)$                                | 0.5                                  | 0.5                    |
| Required final $\sigma(I)$                                    | 0.02                                 | 0.01                   |
| Max. scan time (s)  | 120                                  | 140                    |
| Background measurement  | Equal to half the peak scanning time |                        |
| Standard reflections (no intensity variation)                 | 5, 13, 3 993                         | 264, 153, 244          |
| Collected octants ( $h, k, l$ )                               | + 22, + 33, + 19                     | $\pm$ 11, + 19, + 14   |
| No. of data collected   | 4604                                 | 4805                   |
| No. of independent data                                       | 1522                                 | 1211                   |
|   | [ $I > 2.5\sigma(I)$ ]               | [ $I > 2\sigma(I)$ ]   |
| Equivalent reflections merging                                | 0.0                                  | 0.09                   |
| Absorption correction* range                                  | 1.0–0.45                             | 1.0–0.52               |
| $R$   | 0.058                                | 0.073                  |
| $wR$ †  | 0.060                                | 0.079                  |
| $g$   | 0.001                                | 0.0005                 |
| No. of parameters refined                                     | 195                                  | 173                    |
| Max. $\Delta/\sigma$  | 0.3                                  | 0.2                    |
| Min./max. height in final $\Delta\rho$ (e $\text{\AA}^{-3}$ ) | –0.5/0.43                            | –0.46/0.5              |

\* According to Walker &amp; Stuart (1983).

†  $w = k/[\sigma^2(F) + |g|F^2]$ .Table 2. *Fractional atomic coordinates and thermal parameters ( $\text{\AA}^2$ ) for (1)*

|       | $x$         | $y$         | $z$          | $U_{\text{iso}}$ or $U_{\text{eq}}^*$ |
|-------|-------------|-------------|--------------|---------------------------------------|
| V(1)  | 0.39174 (6) | 0.08520 (4) | 0.07862 (10) | 0.0392 (7)*                           |
| V(2)  | 0.17790 (5) | 0.2500      | 0.25000      | 0.0413 (12)*                          |
| C(1)  | 0.3368 (4)  | 0.0962 (3)  | 0.1951 (6)   | 0.051 (2)                             |
| C(2)  | 0.2898 (4)  | 0.0982 (2)  | 0.1300 (5)   | 0.046 (2)                             |
| C(3)  | 0.2995 (4)  | 0.1275 (2)  | 0.0629 (6)   | 0.047 (2)                             |
| C(4)  | 0.3588 (4)  | 0.1553 (3)  | 0.0625 (6)   | 0.050 (2)                             |
| C(5)  | 0.4079 (4)  | 0.1544 (3)  | 0.1252 (5)   | 0.048 (2)                             |
| C(6)  | 0.3955 (4)  | 0.1246 (2)  | 0.1903 (6)   | 0.052 (2)                             |
| C(7)  | 0.3249 (5)  | 0.0668 (3)  | 0.2668 (6)   | 0.069 (8)*                            |
| C(8)  | 0.2472 (5)  | 0.1308 (3)  | –0.0052 (7)  | 0.070 (7)*                            |
| C(9)  | 0.4692 (4)  | 0.1855 (3)  | 0.1259 (8)   | 0.073 (8)*                            |
| C(10) | 0.4242 (4)  | 0.0141 (3)  | 0.0944 (6)   | 0.052 (2)                             |
| C(11) | 0.3768 (4)  | 0.0165 (3)  | 0.0301 (5)   | 0.048 (2)                             |
| C(12) | 0.3870 (4)  | 0.0459 (3)  | –0.0352 (6)  | 0.054 (2)                             |
| C(13) | 0.4463 (4)  | 0.0737 (3)  | –0.0375 (6)  | 0.058 (3)                             |
| C(14) | 0.4937 (4)  | 0.0722 (3)  | 0.0276 (5)   | 0.051 (2)                             |
| C(15) | 0.4830 (4)  | 0.0422 (2)  | 0.0936 (6)   | 0.058 (3)                             |
| C(16) | 0.4141 (5)  | –0.0190 (3) | 0.1645 (7)   | 0.076 (8)*                            |
| C(17) | 0.3370 (5)  | 0.0466 (4)  | –0.1057 (7)  | 0.090 (9)*                            |
| C(18) | 0.5588 (5)  | 0.1016 (4)  | 0.0245 (9)   | 0.089 (9)*                            |
| C(19) | 0.1390 (4)  | 0.2424 (2)  | 0.3755 (6)   | 0.049 (2)                             |
| C(20) | 0.2117 (3)  | 0.2431 (3)  | 0.3777 (6)   | 0.054 (2)                             |
| C(21) | 0.2507 (5)  | 0.2136 (2)  | 0.3273 (5)   | 0.053 (2)                             |
| C(22) | 0.2167 (4)  | 0.1819 (3)  | 0.2769 (6)   | 0.051 (2)                             |
| C(23) | 0.1439 (4)  | 0.1801 (3)  | 0.2751 (5)   | 0.048 (2)                             |
| C(24) | 0.1058 (4)  | 0.2103 (2)  | 0.3242 (5)   | 0.053 (2)                             |
| C(25) | 0.0981 (4)  | 0.2723 (3)  | 0.4326 (7)   | 0.062 (7)*                            |
| C(26) | 0.3293 (4)  | 0.2137 (3)  | 0.3324 (8)   | 0.072 (8)*                            |
| C(27) | 0.1068 (5)  | 0.1455 (3)  | 0.2214 (7)   | 0.068 (7)*                            |

\*  $U_{\text{eq}} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix})$ .

arene ligands. We described the crystal structure of  $\text{K}[(\eta^6\text{-}1,3,5\text{-C}_6\text{H}_3\text{Me}_3)_2\text{V}]$  in the non-centrosymmetric space group  $P2_1$ , the asymmetric unit containing two independent  $[(\eta^6\text{-}1,3,5\text{-C}_6\text{H}_3\text{Me}_3)_2\text{V}]^-$  anions, two  $\text{K}^+$  cations and two THF and one dioxane solvent molecules. In this paper we report the results of the refinement of the crystal structure of (2) in the centrosymmetric space group  $P2_1/n$  and compare the structural information yielded by the two treatments. We also discuss the structure of the parent 17-electron species  $[(\eta^6\text{-}1,3,5\text{-C}_6\text{H}_3\text{Me}_3)_2\text{V}]$ , focusing attention on the conformational differences between the neutral and the ionic species.

**Experimental.** (1) was synthesized by Fochi, Runjuan & Colligiani (1990), following the procedure of Avilés & Teuben (1983). The synthesis of (2), together with a preliminary discussion of its solid-state structure, has been previously reported (Fochi *et al.*, 1988). In both cases black-brown needles were obtained. The relevant data concerning the crystal structure analyses are summarized in Table 1. The structures were solved by combined use of Patterson and direct methods (Sheldrick, 1986) which allowed location of the V and K atoms. Subsequent difference Fourier maps (SHELX76; Sheldrick 1976) afforded the positions of all other atoms. Full-matrix isotropic refinement (based on  $F$ ) was applied to all atoms except for the V and C(Me) atoms of (1) and V, K and C(Me) atoms of (2), which were treated

anisotropically. Geometrical constraints had to be used for the C—C(Me) bonds of (2). H atoms were partly found on difference Fourier maps and partly located geometrically and refined using a riding model incorporating adequate constraints. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic coordinates are given in Tables 2 and 3 for (1) and (2) respectively.\*

**Discussion.** Fig. 1 shows ORTEP (Johnson, 1965) projections of molecules (1) and (2). The two molecular structures are closely related and will be discussed together.

In (1) one V atom, V(1), occupies a general position, while the other, V(2), lies on a crystallographic twofold axis so that the asymmetric unit contains one and a half molecules. Interestingly, while the mesitylene ligands belonging to V(1) are found almost perfectly eclipsed, there is a slight torsion (*ca*  $5^\circ$ ) of the ligand pairs belonging to V(2). The main packing feature is the nearly orthogonal

\* Lists of structure factors, full listings of bond lengths and angles, anisotropic thermal parameters and H-atom coordinates for both (1) and (2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53279 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates and thermal parameters ( $\text{\AA}^2$ ) for (2)

|       | x            | y           | z            | $U_{\text{iso}}$ or $U_{\text{eq}}^*$ |
|-------|--------------|-------------|--------------|---------------------------------------|
| V(1)  | 0.0560 (2)   | 0.2526 (1)  | -0.1169 (2)  | 0.061 (1)*                            |
| K(1)  | 0.2948 (3)   | 0.1591 (2)  | 0.1369 (2)   | 0.069 (2)*                            |
| C(1)  | 0.0430 (11)  | 0.1660 (7)  | -0.0055 (9)  | 0.060 (4)                             |
| C(2)  | 0.1455 (12)  | 0.1494 (8)  | -0.0746 (10) | 0.068 (4)                             |
| C(3)  | 0.2461 (13)  | 0.1993 (7)  | -0.0957 (10) | 0.070 (4)                             |
| C(4)  | 0.2429 (13)  | 0.2658 (8)  | -0.0435 (10) | 0.075 (4)                             |
| C(5)  | 0.1458 (14)  | 0.2860 (8)  | 0.0256 (11)  | 0.075 (4)                             |
| C(6)  | 0.0439 (12)  | 0.2330 (7)  | 0.0452 (10)  | 0.063 (4)                             |
| C(7)  | -0.0584 (14) | 0.1094 (8)  | 0.0186 (12)  | 0.090 (12)*                           |
| C(8)  | 0.1507 (21)  | 0.3571 (8)  | 0.0808 (13)  | 0.116 (15)*                           |
| C(9)  | 0.3571 (16)  | 0.1802 (11) | -0.1650 (15) | 0.132 (17)*                           |
| C(10) | 0.0527 (13)  | 0.2598 (8)  | -0.2815 (10) | 0.077 (4)                             |
| C(11) | 0.0716 (14)  | 0.3286 (8)  | -0.2402 (11) | 0.078 (4)                             |
| C(12) | -0.0089 (14) | 0.3599 (8)  | -0.1695 (11) | 0.077 (4)                             |
| C(13) | -0.1198 (14) | 0.3184 (8)  | -0.1378 (11) | 0.080 (5)                             |
| C(14) | -0.1454 (11) | 0.2474 (7)  | -0.1735 (10) | 0.063 (3)                             |
| C(15) | -0.0580 (12) | 0.2195 (7)  | -0.2456 (9)  | 0.060 (4)                             |
| C(16) | -0.2634 (12) | 0.2039 (10) | -0.1453 (12) | 0.095 (12)*                           |
| C(17) | 0.0141 (24)  | 0.4362 (8)  | -0.1344 (16) | 0.158 (19)*                           |
| C(18) | 0.1400 (17)  | 0.2290 (11) | -0.3633 (12) | 0.121 (15)*                           |
| O(1)  | -0.3758 (11) | 0.4253 (6)  | -0.2587 (9)  | 0.111 (4)                             |
| O(2)  | -0.0628 (12) | 0.4490 (6)  | -0.4419 (8)  | 0.118 (4)                             |
| C(19) | -0.1274 (12) | 0.5090 (6)  | -0.4694 (8)  | 0.139 (8)                             |
| C(20) | -0.0877 (12) | 0.5359 (6)  | -0.5575 (8)  | 0.146 (8)                             |
| C(21) | -0.4800 (22) | 0.3919 (12) | -0.2043 (16) | 0.147 (8)                             |
| C(22) | -0.5520 (34) | 0.4457 (18) | -0.1578 (25) | 0.239 (14)                            |
| C(23) | -0.4699 (36) | 0.5104 (18) | -0.1585 (31) | 0.245 (14)                            |
| C(24) | -0.3635 (23) | 0.4952 (12) | -0.2223 (18) | 0.148 (8)                             |

\*  $U_{\text{eq}} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$

orientation of the two molecules, as shown by the angle between the normals to the planes passing through the C(1)–C(6) and C(19)–C(24) rings, which is  $97.1^\circ$ .

For (2), the choice of the space group was not straightforward. In our previous paper (Fochi *et al.*, 1988) the structure of (2) was described in the space group  $P2_1$ . Initial attempts in the orthorhombic space group  $P2_12_12_1$  were not successful; after a careful examination of the equivalence conditions this choice was abandoned. The refinement in space group  $P2_1$  led to different rotameric conformations (related by a  $23^\circ$  rotation) of the arene ligands for the two independent molecules in the asymmetric unit. However, the V and K atoms appeared to be almost symmetry related and only a few [and barely significant:  $2\sigma(I) < I < 2.5\sigma(I)$ ]  $h0l$  reflections with  $h + l \neq 2n$  were present. This suggested that the centrosymmetric space group  $P2_1/n$  might be more appropriate for (2). In this space group the asymmetric unit contains one sandwich molecule, one  $\text{K}^+$  cation and one THF molecule in a general position, while the dioxane solvent molecule lies on a crystallographic centre of symmetry. This model converged to  $R = 0.073$  ( $wR = 0.079$ , 173 parameters) compared with  $R = 0.057$  ( $wR = 0.061$ , 244 parameters) for the refinement in  $P2_1$ . The different  $N(\text{obs})/N(\text{var})$  ratios should obviously be taken into account in comparing these agreement indices. The treatment in  $P2_1/n$  leads to a structure for the sandwich anion which is an

average of the two obtained in  $P2_1$ , the rotation angle between the two mesitylene rings being *ca*  $12^\circ$ .

This situation recalls that found in the crystal structure of ferrocene down to 173 K where it has been demonstrated (Seiler & Dunitz, 1979; Takusagawa & Koetzle, 1979) that the molecular centre of symmetry (which relates the staggered cyclopentadienyl ligands) is only statistical in nature, being due to the superposition of four molecules, which could be distinguished below 164 K. In most cases, however, a clear-cut distinction between an ordered structure containing differently oriented molecules and a disordered one containing an 'average' structure can not be made. As pointed out by Marsh (1986), in such cases the centrosymmetric model should be preferred to avoid the near singularities that are inherent to the non-centrosymmetric treatment and that usually lead to poor convergence during refinement. For this reason we have chosen the centrosymmetric model to describe the structure of (2). Probably an accurate X-ray analysis at low

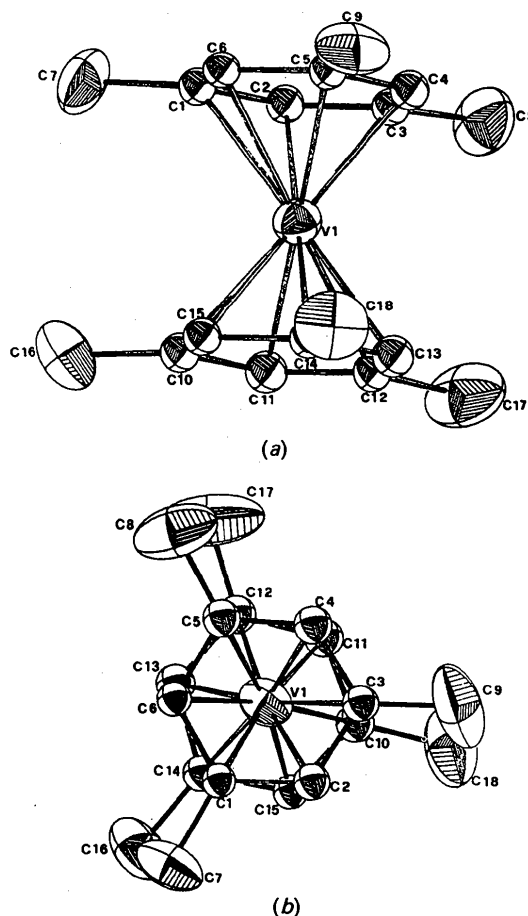


Fig. 1. ORTEP (Johnson, 1965) (50% probability level) views of the structures of (a) (1) (the whole independent molecule), and (b) (2).

Table 4. Bond distances (Å) and angles (°) for (1) and (2) with *r.m.s.* deviations in parentheses

|                                    | (1)       | (2)      |
|------------------------------------|-----------|----------|
| Mean V—C                           |           |          |
| V(1)—C(1-6)                        | 2.20 (1)  | 2.19 (1) |
| V(1)—C(10-15)                      | 2.20 (1)  | 2.19 (1) |
| V(2)—C(19-24)                      | 2.20 (1)  |          |
| Mean C(phenyl)—(phenyl)            |           |          |
| C(1-6)                             | 1.414 (6) | 1.42 (1) |
| C(10-15)                           | 1.412 (9) | 1.41 (2) |
| C(19-24)                           | 1.420 (4) |          |
| Mean C(phenyl)—C(methyl)           |           |          |
| Ring C(1-6)                        | 1.50 (1)  | 1.51 (1) |
| Ring C(10-15)                      | 1.53 (1)  | 1.51 (1) |
| Ring C(19-24)                      | 1.53 (1)  |          |
| K(1)···C(1-6)                      |           | 3.20 (3) |
| K(1)···C(10-15)                    |           | 3.21 (7) |
| K(1)···O(1)                        |           | 2.72 (2) |
| K(1)···O(2)                        |           | 2.68 (2) |
| Mean C(phenyl)—C(phenyl)—C(methyl) |           |          |
| Ring C(1-6)                        | 121 (1)   | 121 (1)  |
| Ring C(10-15)                      | 120 (1)   | 121 (2)  |
| Ring C(19-24)                      | 120 (1)   |          |
| V(1)···K(1)···V(1')                |           | 136.5    |
| V(1)···K(1)···O(1)                 |           | 102.1    |
| V(1')···K(1)···O(1)                |           | 104.9    |
| V(1)···K(1)···O(2)                 |           | 103.5    |
| V(1')···K(1)···O(2)                |           | 106.4    |
| O(1)···K(1)···O(2)                 |           | 96.7     |

temperature is necessary to clarify all aspects of this structural problem.

The eclipsed conformation seems to be generally preferred among bis(arene) sandwiches, notable exceptions being the chromium complexes of bis(trifluoromethyl)benzenes (Muetterties, Bleeke, Wucherer & Albright, 1982). However, due to the small energy difference between the staggered and eclipsed conformations, the intermolecular forces can easily control the molecular structure in the solid state. This behaviour is quite general among bis(arene) and (arene) $M(\text{CO})_3$  complexes, as shown by many structural, spectroscopic and theoretical studies (Muetterties *et al.*, 1982; Albright, Hofmann & Hoffmann, 1977; Albright, 1982). An interesting example of this kind is the complex bis-(2,6-dimethylpyridine)chromium (Riley & Davis, 1976) which crystallizes in two crystal modifications differing in the rotameric conformations of the pyridine rings.

Relevant bond distances and mean values of chemically equivalent bond lengths and angles in (1) and (2) are reported in Table 4. The V—C distances show no appreciable difference between the neutral species and the anion. C(Ph)—C(Ph) and C(Ph)—C(Me) average bond lengths in (1) and (2) are also very similar. However, the rather poor quality of the data does not allow an accurate comparison of the bonding parameters, so that the effect, if any, of the

anionic charge on the structural parameters of (2) cannot be evaluated. The average V—C distances [2.20 (1) and 2.19 (1) Å in (1) and (2), respectively] agree with the values reported for the triple-decker sandwich  $[(\text{C}_5\text{H}_5\text{V})_2(\text{C}_6\text{H}_3\text{Me}_3)]$  [V—C range = 2.193 (3), 2.246 (4) Å (Duff, Jonas, Goddard, Kraus & Kruger, 1983)], containing the same arene. If compared to the other two structurally characterized bis(arene)vanadium(0) complexes, (1) has V—C distances similar to those in  $[\text{V}(\text{C}_6\text{H}_4\text{F}_2)_2]$ , 2.19 (2) Å (Radonovich *et al.*, 1976) and slightly longer than those in  $\text{V}(\text{C}_6\text{H}_6)_2$ , 2.17 Å (Fischer *et al.*, 1963). The arene ligands in both (1) and (2) are essentially parallel to each other [the angles between the arene planes are 0.34° for the independent molecule of (1) and 0.77° for (2)]. Out-of-plane distortions, either towards or away from the metal, of the kind observed in other  $\pi$ -carbocyclic sandwich systems (Radonovich *et al.*, 1976; Radonovich, Koch & Albright, 1980; Swisher, Sinn & Grimes, 1983; Bennet, Matheson, Robertson, Smith & Tucker, 1981) are not detectable. The packing arrangement in (2) shows that each  $\text{K}^+$  cation interacts simultaneously with two mesitylene rings of two neighbouring anions, with one THF and with one dioxane group. This latter molecule, owing to the presence of the centre of symmetry, bridges two contiguous  $\text{K}^+$  cations by using its oxygen termini (Fig. 2). The  $\text{K}^+$ —C distances fall in a narrow range [ $\text{K}\cdots\text{C}(1-6)$  3.20,  $\text{K}\cdots\text{C}(10-15)$  3.21 Å] which compares well with the value of 3.16 (3) Å reported for the system  $[(\text{C}_8\text{H}_8)_2\text{Ce}]^-$  containing a similar contact ion pair

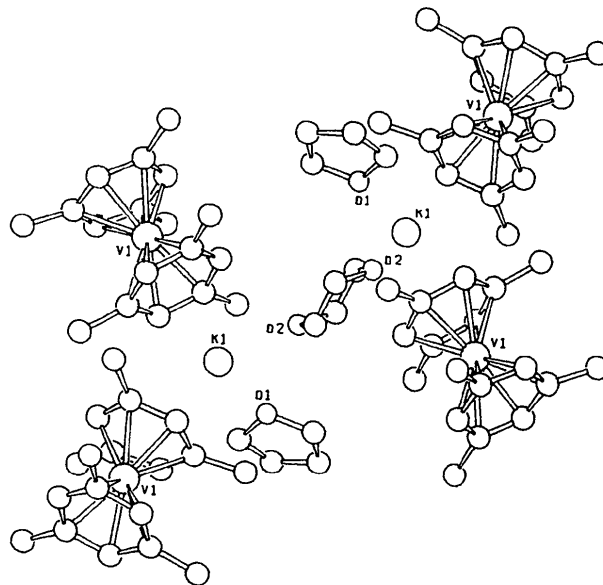


Fig. 2. The crystal structure of (2) showing the bridging dioxane molecule on an inversion centre, and the contact ion pairs established by the sandwich anions and the  $\text{K}^+$  cations.

with K<sup>+</sup> cations (Hodgson & Raymond, 1972). K—O distances [2.72 (2) Å for O(THF) and 2.68 (2) Å for O(dioxane)] are only slightly shorter than in this latter species [K—O(diglyme) 2.792 (5), 2.741 (4) Å]. The coordination geometry around each cation is approximately tetrahedral (see Table 4).

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## Structures of Two Dibenzotetrathiafulvalene (DBTTF) Salts: (DBTTF)Cu(NCS)<sub>2</sub> and a Redetermination of (DBTTF)I<sub>3</sub>

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**Abstract.** 2,2'-Bi-1,3-benzodithiolylianium triiodide (1), C<sub>14</sub>H<sub>8</sub>S<sub>4</sub><sup>+</sup>.I<sub>3</sub><sup>-</sup>, *M<sub>r</sub>* = 685.18, monoclinic, *C*2/*m*, *a* = 19.831 (4), *b* = 9.266 (1), *c* = 14.515 (3) Å, β = 90.03 (2)°, *V* = 2667.2 (8) Å<sup>3</sup>, *Z* = 6, *D<sub>x</sub>* = 2.560 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 56.62 cm<sup>-1</sup>, *F*(000) = 1890, *T* = 295 K, *R* = 0.0434 for 2455 reflections. 2,2'-Bi-1,3-benzodithiolylianium bis(isothiocyanato)cuprate(I), (2), C<sub>14</sub>H<sub>8</sub>S<sub>4</sub><sup>+</sup>.Cu(NCS)<sub>2</sub><sup>-</sup>, *M<sub>r</sub>* = 484.18, triclinic, *P* $\bar{1}$ , *a* = 8.390 (5), *b* = 9.667 (6), *c* = 12.699 (7) Å, α = 95.07 (5), β = 108.25 (5), γ = 112.50 (4)°, *V* = 877.9 (8) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.831 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 19.35 cm<sup>-1</sup>, *F*(000) = 486, *T* = 295 K, *R* = 0.142 for 1647 reflections. In compound (1) the DBTTF ions pack in superimposed triads with short S...S distances of 3.492 (6) Å. The triads are well separated along the triad axis by triiodide ions; however, adjacent triad stacks show S...S con-

tacts of 3.629 (6) Å. There are a number of S...I contacts shorter than the sum of the van der Waals radii, 3.654 (2) to 3.797 (2) Å. In compound (2) the DBTTF ions form infinite stacks with each member of the stack shifted by about a half a molecule from its two neighbors in the stack. The Cu(NCS)<sub>2</sub><sup>-</sup> ions form two infinite two-dimensional sheets between the stacks along the long axes of the DBTTF ions preventing any interstack S...S interactions. The Cu(NCS)<sub>2</sub><sup>-</sup> ions are slightly bent with a 3.055 (9) Å separation between S of one ion and Cu<sup>I</sup> of another.

**Introduction.** There is considerable interest in conducting organic compounds which have highly anisotropic electrical, optical and magnetic properties, and the discovery of superconductivity in some of these systems has heightened this interest. The bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) complexes have generated the most recent interest (Williams *et al.*, 1987) with (BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>

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