# Structural Studies of Eight-co-ordinate Metal Complexes. Part I. Crystal and Molecular Structures of Tetrakis(phenyldithioacetato)vanadium(IV) and Tetrakis(dithiobenzoato)vanadium(IV)

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The structures of tetrakis(phenyldithioacetato)vanadium(IV) (I) and tetrakis(dithiobenzoato)vanadium(IV) (II), have been determined by *X*-ray methods. Crystals of (I) are triclinic, space group $P\bar{1}$, with $a = 9{\cdot}86(3)$, $b = 11{\cdot}395(5)$, $c = 16{\cdot}124(5)$ Å, $\alpha = 77{\cdot}4(4)°$, $\beta = 101{\cdot}0(4)°$, $\gamma = 106{\cdot}1(4)°$, $Z = 2$. The structure was solved from 1831 photographic data by direct methods, and refined by block-diagonal least squares to $R$ 0·119. Crystals of (II) are tetragonal, space group $I4_1/a$, with $a = b = 47{\cdot}887(3)$, $c = 6{\cdot}72(2)$ Å, $Z = 20$. The structure was solved by use of 3120 reflections collected by automatic diffractometer, and by Patterson and Fourier techniques, and refined by least squares to $R$ 0·078. Vanadium is eight-co-ordinate in both compounds, the ligands acting as bidentate chelates. The $VS_8$ co-ordination polyhedra approximate very closely to that of the dodecahedron, with chelation over the *m* edges ($D_{2d}$ $\bar{4}2m$ isomers).

SPECTROCHEMICAL work [1] has suggested that vanadium(IV) dithioates contain eight-co-ordinate $[VS_8]$ chromophores. The present *X*-ray analysis of the structure of (I), tetrakis(phenyldithioacetato)vanadium(IV), gives the first structural proof of the existence of such a chromophore. The structural study of the corresponding dithiobenzoate, (II), was undertaken because of, first, the recent interest in eight-co-ordinate complexes,[2] particularly of metals of low ionic radii,[3] and, secondly, the interest in detailed comparisons between the co-ordination polyhedra, given by ligands having differing π-bonding abilities towards the metal. Preliminary structural features of the two complexes have already been reported.[4]

## EXPERIMENTAL

Both complexes were prepared according to ref. 1, and crystals obtained directly from the reaction mixtures.

The cell dimensions of (I) were determined by an improved version of Christ's method [5] from zero-layer Weissenberg films taken about the *a* axis, and precession photographs about the *b* and *c* axes.

*Crystal Data for* (I).—$C_{32}H_{28}S_8V$, $M = 719{\cdot}99$, Triclinic, $a = 9{\cdot}86(3)$, $b = 11{\cdot}395(5)$, $c = 16{\cdot}124(5)$ Å, $\alpha = 77{\cdot}4(4)°$, $\beta = 101{\cdot}0(4)°$, $\gamma = 106{\cdot}1(4)°$, $U = 1683$ Å$^3$, $D_m = 1{\cdot}42(2)$ (by flotation), $Z = 2$, $D_c = 1{\cdot}42$, $F(000) = 931{\cdot}2$. Cu-$K_\alpha$

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[1] (*a*) O. Piovesana and C. Furlani, *Chem. Comm.*, 1971, 256; (*b*) O. Piovesana and G. Cappuccilli, *Inorg. Chem.*, 1972, **7**, 1543.

[2] S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109.

[3] M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *Chem. Comm.*, 1970, 743; L. Fanfani, A. Nunzi, P. F. Zanazzi, and A. R. Zanzari, *Acta Cryst.*, 1972, **B28**, 1298.

[4] M. Bonamico, G. Dessy, V. Fares, P. Porta, and L. Scaramuzza, *Chem. Comm.*, 1971, 365; M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Cryst. Struct. Comm.*, 1972, **1**, 91.

[5] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.*, 1963, **33** (**IIA**), 1113.

radiation, $\lambda$ = 1·5418 Å; $\mu$(Cu-$K_\alpha$) = 72·0 cm$^{-1}$. Space group $P\bar{1}$ ($C_i^1$, No. 2) from morphology and structure determination.

The intensities of 1831 independent reflections above film background (*ca.* 24% of those possible with Cu-$K_\alpha$ radiation) were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the *a* axis (layers 0—6*kl*) from a prismatic crystal, elongated parallel to the *a* axis, *ca.* 0·07 × 0·03 × 0·01 cm thick. Intensity data were corrected for Lorentz and polarization effects, and for spot extension; absorption and extinction corrections were not applied. Initial scaling was based on the relative exposure times of the different photographs. Independent layer scales were refined during the isotropic phase of the structure refinement.

The *a* cell dimension of (II) was measured from a zero-layer Weissenberg film about the *c* axis by use of the same method;[5] *c* was determined by means of experimental values of equi-inclination angles on an automatic Weissenberg diffractometer.

TABLE 1

Co-ordinates (×10$^4$) and temperature factors,* with standard deviations in parentheses, for (I)

| | $x/a$ | $y/b$ | $z/c$ | $b_{11}$ | $b_{12}$ | $b_{13}$ | $b_{22}$ | $b_{23}$ | $b_{33}$ |
|---|---|---|---|---|---|---|---|---|---|
| V | 6984(4) | 7437(3) | 2315(2) | 154(7) | 83(7) | −10(5) | 144(4) | −52(4) | 56(2) |
| S(1) | 8996(8) | 6435(7) | 2385(5) | 219(14) | 195(18) | 2(11) | 255(10) | −149(10) | 109(4) |
| S(2) | 9244(8) | 8414(10) | 3150(7) | 170(14) | 153(21) | −74(15) | 371(15) | −385(19) | 201(8) |
| S(3) | 6552(8) | 6115(6) | 3713(3) | 339(16) | 205(17) | 34(9) | 202(8) | −34(7) | 59(3) |
| S(4) | 6217(7) | 8537(6) | 3290(4) | 243(13) | 188(15) | −13(9) | 207(8) | −93(7) | 71(3) |
| S(5) | 5785(7) | 5303(5) | 1924(4) | 269(13) | 92(13) | −5(9) | 136(6) | −57(6) | 78(3) |
| S(6) | 4438(7) | 7204(6) | 1758(4) | 173(12) | 76(13) | −36(10) | 170(7) | −93(8) | 115(4) |
| S(7) | 7210(10) | 7715(6) | 770(4) | 504(20) | 143(18) | 99(11) | 154(7) | −25(7) | 63(3) |
| S(8) | 7300(10) | 9629(6) | 1548(4) | 490(19) | 6(17) | 108(12) | 152(7) | −53(7) | 74(3) |

| | $x/a$ | $y/b$ | $z/c$ | $B$ | | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 9993(24) | 7463(19) | 2932(13) | 7·02(47) | C(17) | 4359(24) | 5801(19) | 1588(13) | 7·19(49) |
| C(2) | 11657(30) | 7566(24) | 3221(16) | 9·58(64) | C(18) | 2967(28) | 4941(23) | 1215(16) | 9·05(60) |
| C(3) | 12083(23) | 7593(19) | 4156(12) | 6·64(45) | C(19) | 2181(25) | 5741(19) | 461(12) | 7·10(48) |
| C(4) | 12800(28) | 8752(23) | 4379(16) | 8·98(60) | C(20) | 1099(27) | 6181(21) | 530(14) | 7·79(52) |
| C(5) | 13244(31) | 8759(26) | 5272(18) | 10·54(72) | C(21) | 414(28) | 6894(23) | −171(16) | 8·77(58) |
| C(6) | 12877(37) | 7662(33) | 5861(21) | 12·44(87) | C(22) | 806(29) | 7076(22) | −954(16) | 8·74(59) |
| C(7) | 12204(36) | 6629(31) | 5598(21) | 11·77(82) | C(23) | 1918(31) | 6661(24) | −1045(16) | 9·49(64) |
| C(8) | 11806(31) | 6592(26) | 4759(18) | 9·98(67) | C(24) | 2572(26) | 5935(21) | −343(15) | 7·86(51) |
| C(9) | 6222(22) | 7233(17) | 4047(11) | 6·05(42) | C(25) | 7272(23) | 9208(18) | 651(12) | 6·65(45) |
| C(10) | 5884(24) | 7147(19) | 4949(13) | 7·08(47) | C(26) | 7428(29) | 10099(24) | −213(17) | 9·61(64) |
| C(11) | 7229(22) | 7195(18) | 5551(12) | 6·12(41) | C(27) | 7170(24) | 9448(17) | −980(12) | 6·34(44) |
| C(12) | 8246(27) | 8265(21) | 5523(14) | 7·84(52) | C(28) | 8306(29) | 9450(23) | −1386(16) | 9·21(62) |
| C(13) | 9543(36) | 8497(31) | 6053(21) | 11·90(82) | C(29) | 7942(33) | 8877(27) | −2131(18) | 10·02(67) |
| C(14) | 9819(35) | 7520(31) | 6593(20) | 11·52(79) | C(30) | 6670(38) | 8337(27) | −2361(18) | 10·56(73) |
| C(15) | 8953(35) | 6417(28) | 6730(19) | 10·80(74) | C(31) | 5563(35) | 8245(26) | −2032(19) | 10·70(74) |
| C(16) | 7498(31) | 6170(26) | 6178(18) | 10·30(70) | C(32) | 5801(29) | 8902(23) | −1251(16) | 8·84(59) |

* Exponential coefficients $b_{ij}$ as given here are defined by $T = \exp[10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

*Crystal Data for* (II).—$C_{28}H_{20}S_8V$, $M$ = 663·89, Tetragonal, $a = b$ = 47·887(3), $c$ = 6·72(2) Å, $U$ = 15410 Å$^3$, $D_m$ = 1·44(2) (by flotation), $Z$ = 20, $D_c$ = 1·43, $F(000)$ = 6779·7. Cu-$K_\alpha$ radiation; $\mu$(Cu-$K_\alpha$) = 78·2 cm$^{-1}$. Space group $I4_1/a$ ($C_{4h}^6$, No. 88), from systematic absences and structure determination.

Intensities were measured on a STOE automatic Weissenberg diffractometer, from a crystal (average radius 0·01 cm) mounted along the needle (*c*) axis. Nickel-filtered Cu-$K_\alpha$ radiation was monochromatized by a plane graphite crystal. The $\theta$—$2\theta$ scan technique was used with $\Delta\theta$ 1·50°. All the reflections with $8° < 2\theta < 100°$ were collected. Background for every reflection was determined by two stationary-crystal–stationary-counter measurements at the beginning and end of the scan. One reference reflection for each layer was monitored during collection. Corrections were made for Lorentz and polarization[6] effects, and for absorption. No extinction correction was applied. 3120 Independent reflections (35%) were considered significant having $I > 3C^{\frac{1}{2}}$, where $C$ is the integrated intensity, not corrected for background. Independent layer scales were refined during the isotropic phase of the structure refinement.

*Determination and Refinement of the Structures.*—The structure of (I) was solved by a direct phase-determining procedure based on the iterative application of Sayre's equation. The direct procedure gave the signs of 114 reflections with $1·83 \leqslant |E| \leqslant 4·86$. Several cycles of a 4 × 4 block-diagonal least-squares refinement, with isotropic temperature factors, converged to $R$ 0·179. Anisotropic refinement for vanadium and sulphur atoms (isotropic for carbon atoms) further reduced $R$ to a final value of 0·119. The weighting scheme used was $w = (1·8 + |F_o| + 0·005|F_o|^2)^{-1}$. Final shifts in atomic parameters were all $\leqslant 0·2\sigma$.

The structure of (II) was determined by Patterson and Fourier methods. Space group $I4_1/a$, with 20 molecules in the unit cell, requires that 4 equivalent vanadium atoms be in the special position 4(*a*) or 4(*b*), and 16 equivalent vanadium atoms in the general position 16(*f*). The Patterson map showed the positions of the two independent vanadium atoms and all the sulphur atoms. Successive Fourier maps led to the localization of all the carbon atoms. Refinement by block-diagonal least squares with isotropic temperature factors converged to $R$ 0·126. The final refinement, with anisotropic temperature factors for all non-hydrogen atoms and new independent scales for layers, given by the isotropic refinement, gave $R$ 0·078. Shifts in atomic parameters were $\leqslant 0·01\sigma$. The weighting scheme used was $w = (10·0 + |F_o| + 0·002|F_o|^2)^{-1}$.

Tables 1 and 2 give the final atomic parameters and their standard deviations within the crystal chemical units for

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[6] H. A. Levy and R. D. Ellison, *Acta Cryst.*, 1960, **13**, 270.

both complexes. The values for $b_{11}$, $b_{12}$, and $b_{13}$ in Table 1 and for $b_{13}$, $b_{23}$, and $b_{33}$ in Table 2 are almost without significance, owing to the fact that data were taken about only one axis. The structure factors, based on the final atomic parameters, compared with the observed structure amplitudes, for both compounds, are listed in Supplementary Publication No. SUP 20959 (16 pp., 1 microfiche).* Bond distances and angles within the crystal chemical unit, with their estimated standard deviations, are in Tables 3 and 4.

TABLE 2

Co-ordinates ($\times 10^4$) and temperature factors,* with standard deviations in parentheses, for (II)

| | $x/a$ | $y/b$ | $z/c$ | $b_{11}$ | $b_{12}$ | $b_{13}$ | $b_{22}$ | $b_{23}$ | $b_{33}$ |
|---|---|---|---|---|---|---|---|---|---|
| V(1) | 0(0) | 2500(0) | 1250(2) | 2(0) | 0(0) | 0(0) | 2(0) | 0(0) | 148(7) |
| V(2) | 999(0) | 461(0) | 3269(2) | 2(0) | 0(0) | 0(1) | 3(0) | 1(1) | 164(4) |
| S(1,1) | 37(1) | 2168(1) | 4265(4) | 5(0) | 1(0) | 1(1) | 3(0) | 0(1) | 194(6) |
| S(1,2) | 51(1) | 2011(1) | 228(4) | 7(0) | 1(0) | 2(2) | 3(0) | −1(1) | 195(7) |
| S(2,1) | 924(1) | 776(1) | 6278(4) | 8(0) | 2(0) | 17(2) | 3(0) | 5(1) | 226(7) |
| S(2,2) | 934(1) | 952(1) | 2356(4) | 9(0) | 3(0) | 16(2) | 4(0) | 19(2) | 218(8) |
| S(2,3) | 680(1) | 427(1) | 260(4) | 3(0) | −2(0) | −3(1) | 8(0) | 16(2) | 193(7) |
| S(2,4) | 510(1) | 354(1) | 4166(4) | 3(0) | −1(0) | 1(1) | 9(0) | 21(2) | 213(7) |
| S(2,5) | 1046(1) | 134(1) | 6286(4) | 4(0) | 1(0) | 0(1) | 3(0) | 0(1) | 209(6) |
| S(2,6) | 1093(1) | −21(1) | 2270(4) | 5(0) | 0(0) | −8(2) | 3(0) | −8(1) | 218(7) |
| S(2,7) | 1325(1) | 522(1) | 269(4) | 2(0) | −1(0) | −2(1) | 5(0) | −4(1) | 174(6) |
| S(2,8) | 1483(1) | 542(1) | 4277(4) | 3(0) | −1(0) | −5(1) | 5(0) | 1(1) | 167(6) |
| C(1,1) | 56(2) | 1912(2) | 2561(14) | 2(0) | 1(1) | 7(5) | 4(1) | −17(5) | 177(24) |
| C(1,2) | 66(2) | 1609(2) | 3213(16) | 3(1) | 0(1) | −2(6) | 3(1) | 10(6) | 257(30) |
| C(1,3) | 86(2) | 1531(2) | 5211(16) | 6(1) | 1(1) | −5(7) | 4(1) | 7(6) | 197(30) |
| C(1,4) | 91(3) | 1250(3) | 5767(22) | 10(1) | 1(1) | 10(11) | 4(1) | 15(9) | 401(46) |
| C(1,5) | 82(4) | 1050(3) | 4279(25) | 15(2) | 1(1) | −30(14) | 3(1) | 24(9) | 442(54) |
| C(1,6) | 65(5) | 1121(3) | 2298(29) | 24(2) | 1(2) | −16(19) | 2(1) | −5(10) | 528(66) |
| C(1,7) | 51(4) | 1409(3) | 1688(26) | 19(2) | 1(2) | −25(16) | 3(1) | −36(10) | 452(56) |
| C(2,1) | 895(2) | 1050(2) | 4764(15) | 2(0) | 1(1) | −1(5) | 4(1) | −4(6) | 260(28) |
| C(2,2) | 846(2) | 1335(2) | 5398(18) | 3(1) | 2(1) | −11(7) | 3(1) | 1(7) | 389(38) |
| C(2,3) | 863(3) | 1549(3) | 4034(22) | 7(1) | −1(1) | 2(9) | 5(1) | 28(9) | 386(43) |
| C(2,4) | 802(3) | 1826(3) | 4689(31) | 9(1) | 5(1) | 9(15) | 4(1) | −3(2) | 722(76) |
| C(2,5) | 736(3) | 1876(3) | 6542(32) | 8(1) | 4(2) | −29(14) | 5(1) | −39(13) | 725(78) |
| C(2,6) | 722(3) | 1659(3) | 8039(28) | 8(1) | 6(2) | −31(13) | 7(1) | −67(13) | 600(65) |
| C(2,7) | 773(3) | 1386(3) | 7380(20) | 5(1) | 5(1) | −27(8) | 7(1) | −56(9) | 372(42) |
| C(2,8) | 413(2) | 378(2) | 1778(14) | 3(1) | 1(1) | 1(5) | 3(1) | −1(5) | 177(24) |
| C(2,9) | 117(2) | 367(2) | 1084(15) | 3(1) | 1(1) | −1(6) | 3(1) | −10(6) | 239(28) |
| C(2,10) | 52(2) | 437(3) | −844(19) | 4(1) | 1(1) | −12(7) | 6(1) | −30(8) | 351(39) |
| C(2,11) | −231(3) | 435(3) | −1493(24) | 6(1) | 3(1) | −28(10) | 10(1) | −57(11) | 431(50) |
| C(2,12) | −441(2) | 359(3) | −138(23) | 3(1) | 0(1) | −24(9) | 9(1) | −41(11) | 384(53) |
| C(2,13) | −368(2) | 281(3) | 1753(25) | 3(1) | −2(1) | −7(10) | 7(1) | −2(11) | 566(60) |
| C(2,14) | −91(2) | 282(2) | 2456(21) | 3(1) | −2(1) | 9(8) | 5(1) | −1(8) | 642(43) |
| C(2,15) | 1090(2) | −129(2) | 4669(15) | 3(0) | 1(1) | −2(5) | 3(0) | 24(5) | 236(27) |
| C(2,16) | 1118(2) | −425(2) | 5280(16) | 4(1) | 0(1) | −2(6) | 3(1) | −12(6) | 275(32) |
| C(2,17) | 1119(2) | −497(2) | 7244(18) | 6(1) | 1(1) | 17(7) | 3(1) | 19(6) | 304(36) |
| C(2,18) | 1148(3) | −779(3) | 7884(24) | 9(1) | 2(1) | 8(11) | 5(1) | 11(10) | 432(51) |
| C(2,19) | 1187(4) | −978(2) | 6292(25) | 14(1) | 3(1) | −12(13) | 3(1) | 18(9) | 438(51) |
| C(2,20) | 1216(5) | −901(3) | 4317(33) | 18(2) | 5(2) | 12(20) | 2(1) | 1(12) | 742(83) |
| C(2,21) | 1172(4) | −619(3) | 3808(22) | 16(1) | 2(2) | −36(12) | 4(1) | −16(8) | 289(41) |
| C(2,22) | 1587(2) | 565(2) | 1888(13) | 1(0) | −1(1) | −2(5) | 4(1) | −6(5) | 142(22) |
| C(2,23) | 1885(2) | 606(2) | 1270(16) | 2(1) | −1(1) | −7(6) | 3(1) | −7(6) | 267(31) |
| C(2,24) | 2086(2) | 603(3) | 2719(22) | 2(1) | −4(1) | −2(8) | 13(1) | 2(11) | 381(45) |
| C(2,25) | 2358(3) | 655(4) | 2127(23) | 5(1) | −6(2) | −28(9) | 17(2) | 52(14) | 346(48) |
| C(2,26) | 2438(3) | 690(3) | 209(24) | 4(1) | −4(1) | 4(9) | 8(1) | 27(11) | 478(53) |
| C(2,27) | 2228(2) | 690(2) | −1264(19) | 4(1) | −1(1) | 15(7) | 4(1) | 3(7) | 346(36) |
| C(2,28) | 1946(2) | 651(2) | −709(16) | 4(1) | −2(1) | 16(6) | 4(1) | −13(7) | 260(31) |

* Defined as in footnote to Table 1.

*Calculations.*—Calculations were carried out on the UNIVAC 1108 computer of Rome University, by use of the system of programs of the Laboratorio di Strutturistica Chimica del C.N.R.[7] Specially written programs were also used in the processing of automatic diffractometer data. Scattering factors (neutral atoms) for the listed final structure factors were taken from ref. 8 and corrections for anomalous scattering from ref. 9.

RESULTS AND DISCUSSION

The structures of both complexes consist of discrete monomolecular units, with no non-hydrogen intermolecular contacts $<4{\cdot}05$ Å in (I) and $<3{\cdot}37$ Å in (II). The co-ordination geometry approximates very closely to dodecahedral, with chelation along the *m* edges (*mmmm* subclass, according to the Hoard and Silverton notation [10]).

The pseudo $\bar{4}$ axis of the V(dtpa)$_4$ (I) molecule is parallel to the *y* axis, while the two interlocking trapezoids are roughly parallel to (100) and (001).

In (II) one of the two independent vanadium atoms lies on the $\bar{4}$ axis, which is parallel to *c*. The co-ordina-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[7] A. Domenicano, R. Spagna, and A. Vaciago, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1969, **47**, 331.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[10] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

tion polyhedron in the general position has its pseudo $\bar{4}$ axis also parallel to the unique axis $c$.

The parameters used to describe the shape of the dodecahedra are in Table 5. Since the two independent molecules of (II) are strictly similar, the listed parameters have been determined by averaging over both molecules. Estimated standard deviations, given in parentheses in this Table, have been computed from the spread of values, by use of the formula $\sigma = [\sum_{i=1}^{n}(x_i - \bar{x})^2/(n - 1)]^{\frac{1}{2}}$, where $n$ is number of values of $x_i$, and $\bar{x}$ is the mean value. The least-squares planes computed for both complexes are in Table 6.

TABLE 3

Molecular geometry within the formula unit, with estimated standard deviations in parentheses, for (I)

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| V–S(1) | 2·52(1) | C(9)–C(10) | 1·53(3) |
| V–S(2) | 2·48(1) | C(10)–C(11) | 1·48(3) |
| V–S(3) | 2·46(1) | C(11)–C(12) | 1·35(3) |
| V–S(4) | 2·54(1) | C(11)–C(16) | 1·42(3) |
| V–S(5) | 2·55(1) | C(12)–C(13) | 1·39(4) |
| V–S(6) | 2·46(1) | C(13)–C(14) | 1·32(5) |
| V–S(7) | 2·49(1) | C(14)–C(15) | 1·31(4) |
| V–S(8) | 2·50(1) | C(15)–C(16) | 1·53(4) |
| S(1)–C(1) | 1·61(2) | C(17)–C(18) | 1·55(3) |
| S(2)–C(1) | 1·60(3) | C(18)–C(19) | 1·57(3) |
| S(3)–C(9) | 1·62(2) | C(19)–C(20) | 1·33(4) |
| S(4)–C(9) | 1·71(2) | C(19)–C(24) | 1·38(3) |
| S(5)–C(17) | 1·62(3) | C(20)–C(21) | 1·42(3) |
| S(6)–C(17) | 1·66(2) | C(21)–C(22) | 1·35(4) |
| S(7)–C(25) | 1·66(2) | C(22)–C(23) | 1·35(5) |
| S(8)–C(25) | 1·61(2) | C(23)–C(24) | 1·41(3) |
| C(1)–C(2) | 1·60(4) | C(25)–C(26) | 1·54(3) |
| C(2)–C(3) | 1·49(3) | C(26)–C(27) | 1·52(4) |
| C(3)–C(4) | 1·40(3) | C(27)–C(28) | 1·40(4) |
| C(3)–C(8) | 1·33(3) | C(27)–C(32) | 1·35(3) |
| C(4)–C(5) | 1·42(4) | C(28)–C(29) | 1·43(4) |
| C(5)–C(6) | 1·40(4) | C(29)–C(30) | 1·26(4) |
| C(6)–C(7) | 1·30(5) | C(30)–C(31) | 1·3(1) |
| C(7)–C(8) | 1·34(4) | C(31)–C(32) | 1·55(4) |

(*b*) Angles (°)

| | | | |
|---|---|---|---|
| S(1)–V–S(2) | 66·1(3) | C(12)–C(11)–C(16) | 117(2) |
| S(3)–V–S(4) | 67·8(2) | C(11)–C(12)–C(13) | 127(2) |
| S(5)–V–S(6) | 67·5(2) | C(12)–C(13)–C(14) | 115(3) |
| S(7)–V–S(8) | 66·1(2) | C(13)–C(14)–C(15) | 127(3) |
| V–S(1)–C(1) | 88(1) | C(14)–C(15)–C(16) | 119(3) |
| V–S(2)–C(1) | 89·5(9) | C(11)–C(16)–C(15) | 115(2) |
| V–S(3)–C(9) | 91·1(7) | S(5)–C(17)–S(6) | 116(1) |
| V–S(4)–C(9) | 86·6(8) | S(5)–C(17)–C(18) | 120(2) |
| V–S(5)–C(17) | 86·9(8) | S(6)–C(17)–C(18) | 123(2) |
| V–S(6)–C(17) | 89·0(8) | C(17)–C(18)–C(19) | 108(2) |
| V–S(7)–C(25) | 90·3(8) | C(18)–C(19)–C(20) | 125(2) |
| V–S(8)–C(25) | 90·9(7) | C(18)–C(19)–C(24) | 118(2) |
| S(1)–C(1)–S(2) | 117(1) | C(20)–C(19)–C(24) | 117(2) |
| S(1)–C(1)–C(2) | 122(2) | C(19)–C(20)–C(21) | 123(2) |
| S(2)–C(1)–C(2) | 121(2) | C(20)–C(21)–C(22) | 119(3) |
| C(1)–C(2)–C(3) | 112(2) | C(21)–C(22)–C(23) | 120(2) |
| C(2)–C(3)–C(4) | 116(2) | C(22)–C(23)–C(24) | 120(2) |
| C(2)–C(3)–C(8) | 123(2) | C(19)–C(24)–C(23) | 121(3) |
| C(4)–C(3)–C(8) | 121(2) | S(7)–C(25)–S(8) | 112(1) |
| C(3)–C(4)–C(5) | 116(2) | S(7)–C(25)–C(26) | 123(2) |
| C(4)–C(5)–C(6) | 119(3) | S(8)–C(25)–C(26) | 125(2) |
| C(5)–C(6)–C(7) | 121(3) | C(25)–C(26)–C(27) | 114(2) |
| C(6)–C(7)–C(8) | 121(3) | C(26)–C(27)–C(28) | 121(2) |
| C(3)–C(8)–C(7) | 122(3) | C(26)–C(27)–C(32) | 117(2) |
| S(3)–C(9)–S(4) | 114(1) | C(28)–C(27)–C(32) | 123(2) |
| S(3)–C(9)–C(10) | 124(1) | C(27)–C(28)–C(29) | 116(2) |
| S(4)–C(9)–C(10) | 121(2) | C(28)–C(29)–C(30) | 120(3) |
| C(9)–C(10)–C(11) | 108(2) | C(29)–C(30)–C(31) | 129(3) |
| C(10)–C(11)–C(12) | 119(2) | C(30)–C(31)–C(32) | 116(3) |
| C(10)–C(11)–C(16) | 123(2) | C(27)–C(32)–C(31) | 116(3) |

TABLE 4

Molecular geometry within the asymmetric unit, with estimated standard deviations in parentheses, for (II)

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| V(1)–S(1,1) | 2·580(3) | C(2,2)–C(2,3) | 1·38(2) |
| V(1)–S(1,2) | 2·451(3) | C(2,2)–C(2,7) | 1·40(2) |
| V(2)–S(2,1) | 2·549(3) | C(2,3)–C(2,4) | 1·43(2) |
| V(2)–S(2,2) | 2·449(3) | C(2,4)–C(2,5) | 1·31(3) |
| V(2)–S(2,3) | 2·539(3) | C(2,5)–C(2,6) | 1·45(2) |
| V(2)–S(2,4) | 2·469(3) | C(2,6)–C(2,7) | 1·40(2) |
| V(2)–S(2,5) | 2·572(3) | C(2,8)–C(2,9) | 1·49(1) |
| V(2)–S(2,6) | 2·447(3) | C(2,9)–C(2,10) | 1·37(2) |
| V(2)–S(2,7) | 2·566(3) | C(2,9)–C(2,14) | 1·42(2) |
| V(2)–S(2,8) | 2·447(3) | C(2,10)–C(2,11) | 1·42(2) |
| S(1,1)–C(1,1) | 1·68(1) | C(2,11)–C(2,12) | 1·40(2) |
| S(1,2)–C(1,1) | 1·64(1) | C(2,12)–C(2,13) | 1·37(2) |
| S(2,1)–C(2,1) | 1·66(1) | C(2,13)–C(2,14) | 1·41(2) |
| S(2,2)–C(2,1) | 1·70(1) | C(2,15)–C(2,16) | 1·49(1) |
| S(2,3)–C(2,8) | 1·65(1) | C(2,16)–C(2,17) | 1·36(2) |
| S(2,4)–C(2,8) | 1·68(1) | C(2,16)–C(2,21) | 1·38(2) |
| S(2,5)–C(2,15) | 1·68(1) | C(2,17)–C(2,18) | 1·43(2) |
| S(2,6)–C(2,15) | 1·69(1) | C(2,18)–C(2,19) | 1·44(2) |
| S(2,7)–C(2,22) | 1·67(1) | C(2,19)–C(2,20) | 1·39(3) |
| S(2,8)–C(2,22) | 1·68(1) | C(2,20)–C(2,21) | 1·41(2) |
| C(1,1)–C(1,2) | 1·52(1) | C(2,22)–C(2,23) | 1·50(1) |
| C(1,2)–C(1,3) | 1·40(2) | C(2,23)–C(2,24) | 1·37(2) |
| C(1,2)–C(1,7) | 1·40(2) | C(2,23)–C(2,28) | 1·38(2) |
| C(1,3)–C(1,4) | 1·40(2) | C(2,24)–C(2,25) | 1·38(2) |
| C(1,4)–C(1,5) | 1·38(2) | C(2,25)–C(2,26) | 1·35(2) |
| C(1,5)–C(1,6) | 1·38(3) | C(2,26)–C(2,27) | 1·41(2) |
| C(1,6)–C(1,7) | 1·44(2) | C(2,27)–C(2,28) | 1·41(1) |
| C(2,1)–C(2,2) | 1·45(1) | | |

(*b*) Angles (°)

| | |
|---|---|
| S(1,1)–V(1)–S(1,2) | 68·0(1) |
| V(1)–S(1,1)–C(1,1) | 85·4(3) |
| V(1)–S(1,2)–C(1,1) | 90·6(3) |
| S(1,1)–C(1,1)–S(1,2) | 115·9(5) |
| S(1,1)–C(1,1)–C(1,2) | 120·3(7) |
| S(1,2)–C(1,1)–C(1,2) | 123·7(7) |
| C(1,1)–C(1,2)–C(1,3) | 122·4(9) |
| C(1,1)–C(1,2)–C(1,7) | 116(1) |
| C(1,2)–C(1,3)–C(1,4) | 121(1) |
| C(1,3)–C(1,2)–C(1,7) | 121(1) |
| C(1,3)–C(1,4)–C(1,5) | 118(1) |
| C(1,4)–C(1,5)–C(1,6) | 122(1) |
| C(1,5)–C(1,6)–C(1,7) | 121(1) |
| C(1,2)–C(1,7)–C(1,6) | 116(1) |
| S(2,1)–V(2)–S(2,2) | 67·2(1) |
| S(2,3)–V(2)–S(2,4) | 67·1(1) |
| S(2,5)–V(2)–S(2,6) | 68·0(1) |
| S(2,7)–V(2)–S(2,8) | 67·8(1) |
| V(2)–S(2,1)–C(2,1) | 89·6(4) |
| V(2)–S(2,2)–C(2,1) | 92·3(3) |
| V(2)–S(2,3)–C(2,8) | 89·1(3) |
| V(2)–S(2,4)–C(2,8) | 91·0(3) |
| V(2)–S(2,5)–C(2,15) | 87·5(3) |
| V(2)–S(2,6)–C(2,15) | 91·4(3) |
| V(2)–S(2,7)–C(2,22) | 87·7(3) |
| V(2)–S(2,8)–C(2,22) | 91·4(3) |
| S(2,1)–C(2,1)–S(2,2) | 110·9(5) |
| S(2,1)–C(2,1)–C(2,2) | 125·1(8) |
| S(2,2)–C(2,1)–C(2,2) | 123·9(8) |
| S(2,3)–C(2,8)–S(2,4) | 112·6(5) |
| S(2,3)–C(2,8)–C(2,9) | 123·2(7) |
| S(2,4)–C(2,8)–C(2,9) | 124·2(7) |
| S(2,5)–C(2,15)–S(2,6) | 113·0(5) |
| S(2,5)–C(2,15)–C(2,16) | 123·4(8) |
| S(2,6)–C(2,15)–C(2,16) | 123·6(7) |
| S(2,7)–C(2,22)–S(2,8) | 113·0(5) |
| S(2,7)–C(2,22)–C(2,23) | 123·3(7) |
| S(2,8)–C(2,22)–C(2,23) | 123·6(7) |
| C(2,1)–C(2,2)–C(2,3) | 120(1) |
| C(2,1)–C(2,2)–C(2,7) | 119(1) |
| C(2,2)–C(2,3)–C(2,4) | 118(1) |
| C(2,3)–C(2,2)–C(2,7) | 121(1) |
| C(2,3)–C(2,4)–C(2,5) | 121(2) |
| C(2,4)–C(2,5)–C(2,6) | 123(1) |
| C(2,5)–C(2,6)–C(2,7) | 116(2) |

TABLE 4 (*Continued*)

| | |
|---|---|
| C(2,2)–C(2,7)–C(2,6) | 120(1) |
| C(2,8)–C(2,9)–C(2,10) | 199·9(9) |
| C(2,8)–C(2,9)–C(2,14) | 118·3(9) |
| C(2,9)–C(2,10)–C(2,11) | 120(1) |
| C(2,10)–C(2,9)–C(2,14) | 121·8(9) |
| C(2,10)–C(2,11)–C(2,12) | 119(1) |
| C(2,11)–C(2,12)–C(2,13) | 119(1) |
| C(2,12)–C(2,13)–C(2,14) | 123(1) |
| C(2,9)–C(2,14)–C(2,13) | 116(1) |
| C(2,15)–C(2,16)–C(2,17) | 120·5(9) |
| C(2,15)–C(2,16)–C(2,21) | 117(1) |
| C(2,16)–C(2,17)–C(2,18) | 122(1) |
| C(2,17)–C(2,16)–C(2,21) | 122(1) |
| C(2,17)–C(2,18)–C(2,19) | 115(1) |
| C(2,18)–C(2,19)–C(2,20) | 123(1) |
| C(2,19)–C(2,20)–C(2,21) | 118(2) |
| C(2,16)–C(2,21)–C(2,20) | 120(1) |
| C(2,22)–C(2,23)–C(2,24) | 118(1) |
| C(2,22)–C(2,23)–C(2,28) | 119·4(9) |
| C(2,23)–C(2,24)–C(2,25) | 117(1) |
| C(2,24)–C(2,23)–C(2,28) | 122(1) |
| C(2,24)–C(2,25)–C(2,26) | 124(1) |
| C(2,25)–C(2,26)–C(2,27) | 118(1) |
| C(2,26)–C(2,27)–C(2,28) | 120(1) |
| C(2,23)–C(2,28)–C(2,27) | 119(1) |

TABLE 5

Stereochemical parameters of the dodecahedra

| | (I) | (II) |
|---|---|---|
| V–$S_A$ | 2·53(2) Å | 2·56(2) Å |
| V–$S_B$ | 2·47(1) Å | 2·45(1) Å |
| V–$S_A$/V–$S_B$ | 1·02 | 1·04 |
| $\theta_A$ | 37·5(2)° | 37·9(3)° |
| $\theta_B$ | 76·0(4)° | 74·4(6)° |
| *a* edge | 3·08(1) Å | 3·15(2) Å |
| *b* edge | 3·57 Å [a] | 3·59(7) Å |
| *g* edge | 3·20(10) Å | 3·15(4) Å |
| *m* edge | 2·76(4) Å | 2·79(2) Å |

[a] Single values differ considerably from the mean: 4·10, 3·28, 3·28, 3·60 Å, σ 0·01 Å.

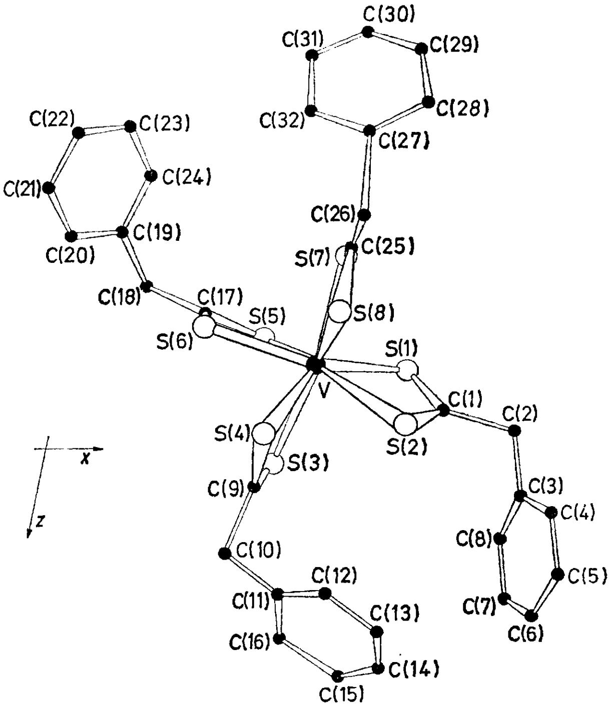

FIGURE 1 [010] projection of the molecule of (I)

TABLE 6

Results of least-squares planes calculation. The equations of the planes, calculated using fractional co-ordinates for the atoms, are referred to the unit-cell axes. The deviations (Å) of the atoms from the planes are given in square brackets

(*a*) For (I)

(i) Plane of dodecahedral trapezoid $T_1$: S(1), S(2), V, S(5), S(6)

$$-2{\cdot}64x - 2{\cdot}78y + 14{\cdot}01z + 0{\cdot}58 = 0$$

[S(1) 0·251, S(2) −0·204, V 0·096, S(5) −0·267, S(6) 0·124]

(ii) Plane of dodecahedral trapezoid $T_2$: S(3), S(4), V, S(7), S(8)

$$8{\cdot}85x + 0{\cdot}39y + 3{\cdot}16z - 7{\cdot}11 = 0$$

[S(3) −0·103, S(4) 0·233, V −0·095, S(7) 0·183, S(8) −0·217]

Dihedral angle $T_1,T_2$: 87·6°

(*b*) For (II)

(i) Plane of dodecahedral trapezoid $T_1$: S(1,1), S(1,2), V(1), S(1,$1^{II}$), S$(1,2)^{II}$

$$47{\cdot}62x + 5{\cdot}03y - 1{\cdot}26 = 0$$

[S(1,1) −0·008, S(1,2) 0·005, V(1) 0·000, S(1,$1^{II}$) 0·007, S(1,$2^{II}$) −0·005]

(ii) Plane of dodecahedral trapezoid $T_2$: S(2,1), S(2,2), V(2), S(2,5), S(2,6)

$$47{\cdot}14x + 8{\cdot}06y + 0{\cdot}34z - 5{\cdot}22 = 0$$

[S(2,1) 0·024, S(2,2) −0·029, V(2) 0·028, S(2,5) −0·031, S(2,6) 0·007]

(iii) Plane of dodecahedral trapezoid $T_3$: S(2,3), S(2,4), V(2), S(2,7), S(2,8)

$$-8{\cdot}46x + 47{\cdot}09y + 0{\cdot}29z - 1{\cdot}40 = 0$$

[S(2,3) −0·046 S(2,4) 0·041, V(2) −0·023, S(2,7) 0·051, S(2,8) −0·023]

Dihedral angle $T_2,T_3$: 89·6°

(iv) Planes of chelating part of ligands:

$C_1$: S(1,1), S(1,2), C(1,1), C(1,2)

$$47{\cdot}83x + 2{\cdot}37y + 0{\cdot}07z - 0{\cdot}72 = 0$$

$C_2$: S(2,1), S(2,2), C(2,1), C(2,2)

$$47{\cdot}22x + 7{\cdot}31y + 0{\cdot}44z - 5{\cdot}21 = 0$$

$C_3$: S(2,3), S(2,4), C(2,8), C(2,9)

$$-4{\cdot}09x + 47{\cdot}45y + 0{\cdot}71z - 1{\cdot}76 = 0$$

$C_4$: S(2,5), S(2,6), C(2,15), C(2,16)

$$47{\cdot}50x + 5{\cdot}56y + 0{\cdot}35z - 5{\cdot}26 = 0$$

$C_5$: S(2,7), S(2,8), C(2,22), C(2,23)

$$-7{\cdot}23x + 47{\cdot}34y + 0{\cdot}05z - 1{\cdot}52 = 0$$

(v) Planes of the phenyl rings:

$P_1$: C(1,1), C(1,2), C(1,3), C(1,4), C(1,5), C(1,6), C(1,7)

$$-47{\cdot}78x - 0{\cdot}57y + 0{\cdot}44z + 0{\cdot}26 = 0$$

$P_2$: C(2,1), C(2,2), C(2,3), C(2,4), C(2,5), C(2,6), C(2,7)

$$46{\cdot}38x + 5{\cdot}79y + 1{\cdot}46z - 5{\cdot}47 = 0$$

$P_3$: C(2,8), C(2,9), C(2,10), C(2,11), C(2,12), C(2,13), C(2,14)

$$-5{\cdot}35x + 45{\cdot}58y + 1{\cdot}92z - 1{\cdot}82 = 0$$

$P_4$: C(2,15), C(2,16), C(2,17). C(2,18), C(2,19), C(2,20), C(2,21)

$$47{\cdot}20x + 6{\cdot}97y + 0{\cdot}57z - 5{\cdot}32 = 0$$

$P_5$: C(2,22), C(2,23), C(2,24), C(2,25), C(2,26), C(2,27), C(2,28)

$$-5{\cdot}53x + 47{\cdot}23y + 0{\cdot}79z - 1{\cdot}93 = 0$$

Dihedral angles: $C_1,P_1$: 4·9°; $C_2,P_2$: 8·9°; $C_3,P_3$: 10·7°; $C_4,P_4$: 2·6°; $C_5,P_5$: 6·6°.

Roman superscript numeral II refers to the following equivalent position: $-x, \frac{1}{2} - y, z$.

Figure 1 shows that the phenyl rings of (I) bonded to C(2) and C(10), respectively, approach each other with their planes roughly perpendicular. A similar effect occurs for the other two phenyl rings. In both cases this effect is due to repulsions between molecules of adjacent unit cells.

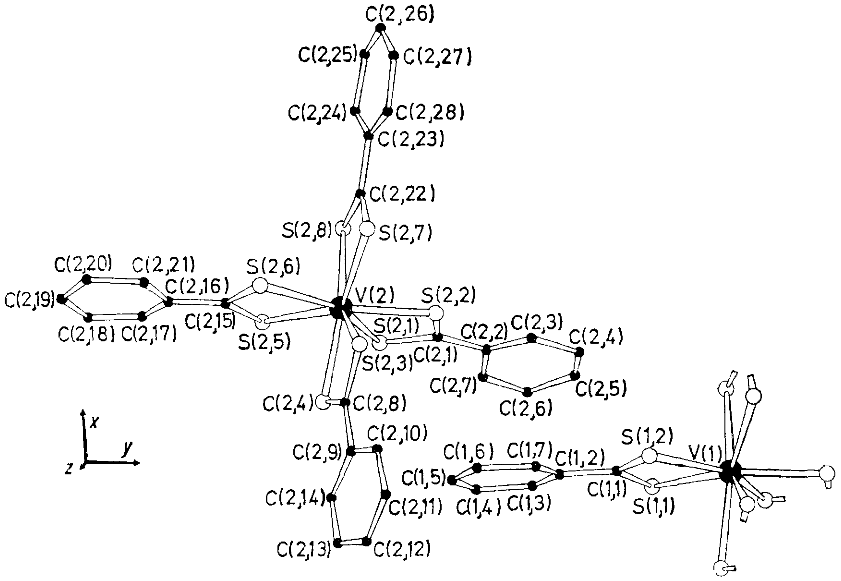

FIGURE 2 Projection of the asymmetric unit of (II) onto the plane of equation $0{\cdot}2608x + 0{\cdot}26086y + 0{\cdot}92946z - 3{\cdot}123 = 0$

Figure 2 shows the asymmetric unit of (II). The angles between the least-squares planes of the chelating part of the ligands $[\text{-C·C(:S)S}^{-}]$ and the phenyl rings are small, the widest being 10·71°. A delocalized bond, involving the whole ligand molecule is then possible, but this feature seems not to have any influence on the co-ordination geometry, which is substantially the same as that of (I). Several authors [10–12] have pointed out that the donor atoms at *B* vertices may form a $d_{\pi}$–$p_{\pi}$ bond with the $d_{x^2-y^2}$ orbitals of the metal. Our results show that V–$S_B$ bond distances and $\theta_B$ angles are not significantly different in the two complexes. We believe that the metal–ligand $\pi$ -bond has only a weak influence on the shape of the co-ordination polyhedra of our complexes, the primary factor being ligand–ligand repulsions. Blight and Kepert [13] calculated the shape of the co-ordination polyhedra, corresponding to the minimum ligand–ligand repulsive energy, for eight-co-ordinate complexes. There is good agreement between our experimental results and some angular parameters computed in ref. 13. If a strong $d_{\pi}$–$p_{\pi}$ bond were present, then it might be expected that the $S_B$ atoms approach more closely towards the equatorial plane, *i.e.* the $\theta_B$ angle should be greater than that calculated assuming only interligand repulsions. However, the experimental $\theta_B$ angles (76 and 74°) agree very well with those calculated (75°) according to ref. 13. Although electronic spectra of these complexes [1b] show strong mixing of valence orbitals of the metal and of the ligands, there is no structural evidence that the bonds influence the stereochemistry of the $[\text{VS}_8]$ chromophore in the two compounds.

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