

Table 6. Distances (Å) from the ring atoms and the coordinated metal atoms to the least-squares planes (of non-hydrogen trz atoms) of the Metrz groups in $Mn_2(Metrz)_5(NCS)_4$

The equations of the planes in direct space are:

$$\begin{aligned} \text{Ring 1: } & -0.1782X + 0.3844Y - 0.9058Z + 8.2625 = 0 \\ \text{Ring 2: } & -0.0535X - 0.9986Y + 14.4558 = 0 \\ \text{Ring 3: } & -0.7462X - 0.1447Y + 0.6498Z + 6.2731 = 0. \end{aligned}$$

	Ring 1	Ring 2	Ring 3
N(1)	0.001 (1)	0.003 (1)	-0.003 (1)
N(2)	-0.001 (1)	-0.003 (1)	0.004 (2)
C(3)	0.001 (2)	0.002 (2)	-0.004 (2)
N(4)	-0.000 (1)	0.0000 (5)	0.001 (2)
C(5)	-0.000 (2)	-0.002 (2)	0.002 (2)
C(6)	-0.018 (2)	0.0000 (6)	-0.043 (2)
H(3)	-0.00 (2)	0.06 (2)	-0.14 (2)
H(5)	-0.01 (2)	-0.06 (2)	-0.15 (2)
Mn	0.232 (1)	0.000 (1)	-0.183 (1)
Mn'	0.426 (1)	0.000 (1)	

* Related to the unprimed Mn by a rotation about the twofold axis.

attached to C atoms, it is unlikely that they are involved in hydrogen bonding; therefore intermolecular bonding will probably be of the van der Waals type.

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Table 7. Intermolecular distances (Å) (≤ 3.5 Å) between neighbouring dimeric units in $Mn_2(Metrz)_5(NCS)_4$

S(1)—H(2,3)	2.81 (4)	S(2)—H2(2,6)	2.98 (6)
—H(3,5)	2.93 (4)	—H1(1,6)	3.16 (5)
—H1(2,6)	2.95 (5)	—H(2,3)	3.26 (4)
—H(3,3)	3.23 (4)	—H1(2,6)	3.32 (5)
—H(1,5)	3.33 (4)	—H2(3,6)	3.41 (5)
—H2(3,6)	3.47 (5)		

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The Structure of Tetraphenylphosphonium Dioxo[4-(2-pyridylazo)-resorcinolato]vanadate(V), $C_{24}H_{20}P^+ \cdot C_{11}H_7N_3O_4V^-$

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Abstract

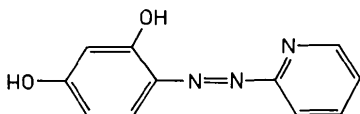
$[P(C_6H_5)_4][V(C_{11}H_7N_3O_2)_2]$, $[Ph_4P][VO_2par]$, is monoclinic, space group $P2_1/c$, with $a = 9.264$ (5), $b = 18.28$ (1), $c = 17.50$ (1) Å, $\beta = 95.10$ (3)°; $Z = 4$, $D_m = 1.430$, $D_c = 1.430$ Mg m⁻³. The structure has been

refined to $R = 0.036$ for 4555 counter reflections with $I > 2\sigma(I)$. The V atom has a pentagonal environment of two oxo O atoms, the phenolic O atom, the azo N atom adjacent to the resorcinol ring, and the pyridine N atom. Thus, two five-membered chelate rings are formed with par acting as a terdentate ligand. The VO_2

group has a bent configuration, with $O-V-O = 109.3$ (1)° and $V-O$ lengths of 1.615 (2) and 1.625 (2) Å. The double-bond character of the azo group is significantly reduced. The $N-N$ length of 1.323 (3) Å and the adjacent $C-N$ lengths of 1.325 (4) and 1.362 (4) Å are all between single- and double-bond lengths. The crystal structure results agree with the IR and 1H NMR spectral measurements.

Introduction

4-(2-Pyridylazo)resorcinol, H_2par ,



is a widely used spectrophotometric reagent and metallochromic indicator. Several papers deal with its analytical application and with studies of complex species in solution. However, few par complexes have been studied in the solid state (Geary, Nickless & Pollard, 1962*b*; Široki & Djordjević, 1971; Široki, Marić, Štefanac & Herak, 1975; Široki, Marić & Herak, 1976), and this is the first report of a structure analysis. Of the par complexes isolated in the solid state, the V complex was chosen as the most appropriate for a structural study. Its structure is of interest with respect to the mode of azo-ligand coordination and the stereochemical parameters of the VO_2 group.

4-(2-Pyridylazo)resorcinol reacts with metal ions giving 1:1 or 1:2 metal-to-ligand complexes. V^V forms only 1:1 chelates $VO_2(Hpar)$ and $[VO_2(par)]^-$ depending on pH. The former complex can be precipitated from aqueous solution at $pH < 4$ as an amorphous solid. It is unstable and decomposes during recrystallization. Several attempts to obtain crystalline $VO_2(Hpar)$ were unsuccessful. On the other hand, the anionic $[VO_2par]^-$ species predominant in solution under the conditions of spectrophotometric determination can be isolated as a stable crystalline compound with tetraphenylphosphonium and -arsonium cations. In this paper the structure analysis of the $[Ph_4P][VO_2par]$ complex is reported and the results are correlated with those obtained by the spectrometric method.

Experimental

Crystalline tetraphenylarsonium and -phosphonium dioxo(par)vanadate(V) were prepared according to the procedure described by Široki & Djordjević (1977).

IR spectra were recorded on a Perkin Elmer spectrophotometer Model 180 in the region $4000-200\text{ cm}^{-1}$ as

Nujol mulls and 1H NMR spectra with a Varian A-60 MHz instrument. X-ray powder photographs were taken with a Philips camera and $Cu K\alpha$ radiation. From the powder photographs as well as from X-ray oscillation and Weissenberg photographs the tetraphenylarsonium and -phosphonium derivatives seemed to be isostructural. Cell dimensions of the arsonium compound were: $a = 9.32$, $b = 18.34$, $c = 17.52$ Å, $\beta = 95^\circ$, $V = 2983$ Å³ (space group $P2_1/c$); $D_m = 1.485$, $D_c = 1.51$ Mg m⁻³, $Z = 4$. The phosphonium compound was selected for structure determination. Well formed single crystals were obtained from ethanol-ether; they were of perfect prismatic shape and dark violet in colour.

The cell dimensions and space group were determined from oscillation and Weissenberg photographs and refined by single-crystal diffractometry. Intensities were collected from a crystal ground to a sphere of $r = 0.18$ mm on a Philips PW 1100 automatic four-circle diffractometer with $Mo K\alpha$ radiation and the $\theta-2\theta$ scanning technique with a scan range of 1.6° and a scan rate of 0.04° s^{-1} .

Crystal data

$C_{24}H_{20}P^+ \cdot C_{11}H_7N_3O_4V^-$, $M_r = 635.5$, monoclinic, $a = 9.264$ (5), $b = 18.28$ (1), $c = 17.50$ (1) Å, $\beta = 95.10$ (3)°, $V = 2952.0$ Å³, $D_m = 1.430$ (by flotation in a mixture of CCl_4 and benzene), $D_c = 1.430$ Mg m⁻³, $Z = 4$, $F(000) = 1312$; space group $P2_1/c$ from absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$; $\mu(Mo K\alpha\text{ radiation}) = 0.4683\text{ mm}^{-1}$.

4976 reflections were measured up to $\sin \theta/\lambda = 0.71$ Å⁻¹, including 182 symmetry-related pairs. Of the 4794 unique reflections (the symmetry-related pairs were averaged), 239 with $I < 2\sigma(I)$ were classified as unobserved.

Corrections were made for Lorentz and polarization factors and for absorption ($\mu_r = 0.083$) with the ZOK program (Vicković, 1975). All calculations were performed on a Univac 1110 computer at the University of Zagreb.

Structure determination and refinement

The V and P atoms were determined by the heavy-atom method, and all other atoms from difference maps. Isotropic least-squares refinement of non-hydrogen atoms gave an R of 0.085 and with H atoms included an R of 0.073. The final R of 0.036 was obtained by refinement with anisotropic thermal parameters for non-hydrogen and isotropic thermal parameters for H atoms.* Full-matrix and block-diagonal refinements

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34701 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional parameters ($\times 10^4$; for V and P $\times 10^5$; for H $\times 10^3$)

	x	y	z
V	84479 (4)	33997 (2)	63949 (3)
P	75973 (6)	39453 (3)	32699 (4)
O(1)	8262 (2)	4120 (1)	5862 (1)
O(2)	6857 (2)	3091 (1)	6555 (1)
O(3)	9070 (2)	2642 (1)	5718 (1)
O(4)	12816 (3)	1013 (1)	5204 (1)
N(1)	8818 (2)	3918 (1)	7453 (1)
N(2)	11183 (2)	3442 (1)	7514 (1)
N(3)	10578 (2)	3125 (1)	6885 (1)
C(1)	6569 (2)	3196 (1)	3601 (2)
C(2)	6038 (3)	2639 (1)	3108 (2)
C(3)	5329 (3)	2052 (1)	3409 (2)
C(4)	5166 (3)	2010 (2)	4187 (2)
C(5)	5717 (3)	2558 (2)	4675 (2)
C(6)	6416 (3)	3153 (1)	4385 (2)
C(7)	7276 (3)	4732 (1)	3836 (2)
C(8)	5842 (3)	4942 (2)	3904 (2)
C(9)	5565 (3)	5586 (2)	4277 (2)
C(10)	6698 (4)	6009 (2)	4592 (2)
C(11)	8116 (3)	5789 (2)	4546 (2)
C(12)	8414 (3)	5153 (1)	4167 (2)
C(13)	7112 (3)	4157 (1)	2281 (2)
C(14)	7604 (3)	3712 (1)	1714 (2)
C(15)	7284 (3)	3876 (2)	950 (2)
C(16)	6480 (3)	4487 (2)	736 (2)
C(17)	5983 (4)	4931 (2)	1289 (2)
C(18)	6294 (3)	4777 (2)	2058 (2)
C(19)	9474 (2)	3694 (1)	3358 (2)
C(20)	9958 (3)	3088 (1)	3774 (2)
C(21)	11418 (3)	2907 (2)	3822 (2)
C(22)	12374 (3)	3336 (2)	3470 (2)
C(23)	11904 (3)	3943 (2)	3058 (2)
C(24)	10449 (3)	4125 (2)	2990 (2)
C(25)	7798 (3)	4315 (2)	7778 (2)
C(26)	8078 (4)	4684 (2)	8452 (2)
C(27)	9468 (4)	4641 (2)	8829 (2)
C(28)	10506 (4)	4228 (2)	8520 (2)
C(29)	10171 (3)	3864 (1)	7822 (2)
C(30)	11278 (3)	2644 (1)	6489 (2)
C(31)	12740 (3)	2391 (2)	6640 (2)
C(32)	13237 (3)	1862 (2)	6209 (2)
C(33)	12332 (3)	1523 (2)	5580 (2)
C(34)	10888 (3)	1804 (2)	5418 (2)
C(35)	10378 (3)	2351 (1)	5842 (2)
H(2)	610 (3)	266 (1)	254 (1)
H(3)	496 (3)	165 (1)	303 (1)
H(4)	468 (3)	158 (2)	439 (2)
H(5)	562 (3)	251 (1)	518 (1)
H(6)	682 (2)	354 (1)	473 (1)
H(8)	505 (3)	460 (2)	368 (2)
H(9)	463 (3)	572 (2)	430 (2)
H(10)	655 (3)	650 (2)	488 (2)
H(11)	896 (3)	610 (2)	483 (2)
H(12)	941 (3)	499 (1)	413 (2)
H(14)	816 (3)	328 (1)	186 (1)
H(15)	766 (3)	359 (2)	54 (2)
H(16)	627 (3)	462 (2)	18 (2)
H(17)	541 (4)	535 (2)	113 (2)
H(18)	603 (3)	510 (2)	246 (2)
H(20)	931 (3)	280 (2)	402 (2)
H(21)	1175 (3)	248 (2)	413 (2)
H(22)	1340 (3)	323 (2)	351 (2)
H(23)	1263 (3)	422 (2)	276 (2)
H(24)	1012 (3)	454 (2)	269 (2)
H(25)	684 (3)	434 (2)	746 (2)

Table 1 (cont.)

	x	y	z
H(26)	735 (3)	501 (2)	864 (2)
H(27)	969 (4)	488 (2)	939 (2)
H(28)	1149 (3)	413 (2)	878 (2)
H(31)	1333 (3)	259 (2)	708 (2)
H(32)	1422 (3)	169 (2)	632 (2)
H(34)	1028 (3)	160 (1)	501 (2)

were used. The last three cycles were by full-matrix refinement varying separately the non-hydrogen atoms from the cation, then those from the anion, and finally the H atoms, while the remaining atoms were treated as fixed atom contributors. Scattering factors of Cromer & Mann (1968) were used for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for hydrogen. The calculations were performed with the XRAY system (Stewart, Ammon, Dickinson & Hall, 1972) and ORXFLS3 program (Busing, Martin & Levy, 1971). E.s.d.'s of deviations of the atoms from their least-squares planes were calculated with programs developed by Domenicano, Spagna & Vaciego (1969). The final atomic coordinates are listed in Table 1. Almost all parameter shifts in the final cycle were $< 0.1\sigma$.

Description and discussion of the structure

Figs. 1 and 2 are schematic drawings of the dioxo(par)-vanadate(V) anion and the tetraphenylphosphonium cation showing bond lengths and angles. The V atom has a pentagonal environment: the two oxo O atoms, the phenolic O, the azo N adjacent to the resorcinol ring, and the pyridine N atoms. par thus acts as a terdentate ligand forming two five-membered chelate rings confirming the assumption based on comparative spectrophotometric studies (Geary, Nickless & Pollard, 1962a).

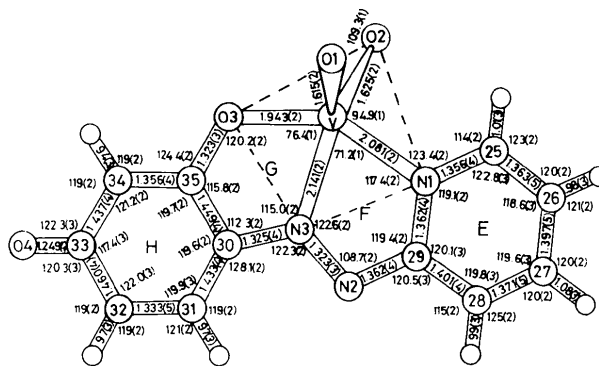


Fig. 1. A schematic drawing of the dioxo(par)vanadate(V) anion showing the bond lengths (Å) and angles ($^{\circ}$). E.s.d.'s are given in parentheses. H atoms are represented by open circles whose numbering is the same as that of the corresponding C atoms. The basal plane of a tetragonal pyramid of the V polyhedron is outlined with dashed lines.

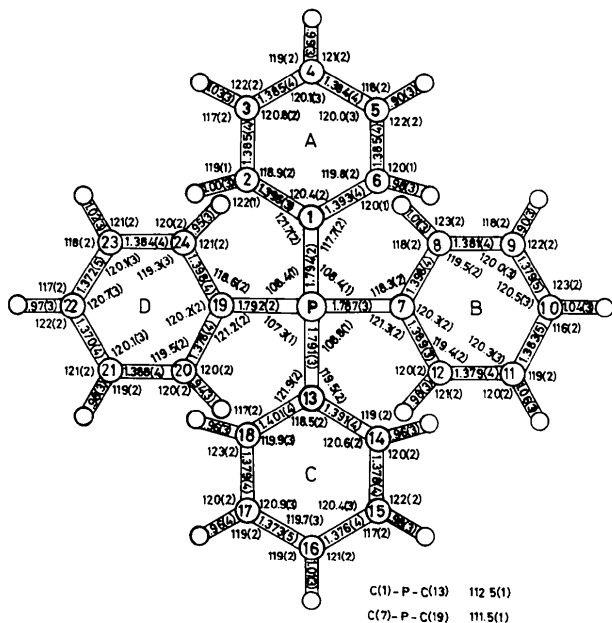


Fig. 2. A schematic drawing of the tetraphenylphosphonium cation showing the bond lengths (Å) and angles ($^{\circ}$). E.s.d.'s are given in parentheses. H atoms are represented by open circles whose numbering is the same as that of the corresponding C atoms. [C(1)–C(2) 1.396 (3) Å.]

Muetterties & Schunn (1966) pointed out that the possibility of constraints involved by steric requirements of polydentate ligands invalidates any consideration based on idealized geometries. The distances and angles of the V polyhedron shown in Fig. 1 and Table 2 are distinctly nearer to a tetragonal pyramid, although very distorted [O(1) in the apical position], than to a trigonal bipyramid [O(3) and N(1) in the apical positions]. Strong deviations of the basal-plane atoms from planarity (Table 3) indicate a tetrahedral distortion. The angle between the O(1)–V bond and the normal to the basal plane is 7.6° . The V atom is displaced from the centre of gravity toward the pair of oxo ligands, and is 0.546 Å above the plane of the basal atoms. However, the angle between the mean planes through O(1), O(2), N(3), V and O(1), N(1), O(3), V is 89.1° , close to the theoretical angle of 90° . If the trigonal bipyramidal polyhedron is considered, the three angles between planes through the apical O(3) and N(1), the V atom and the equatorial O(1), O(2), and N(3) are 32.7 , 52.6 and 85.3° respectively, considerably further from the theoretical value of 60° . Another interpretation, by a tetrahedron with two N atoms in one corner is perhaps a better approximation of the actual V polyhedron. Six tetrahedral angles between V, O(1), O(2), O(3) and the point *M* bisecting the N(1)–N(3) distance range from 100.4 to 117.9° (Table 2). The angle between the plane defined by O(1) and V and the plane through O(2), V, O(3) is 90.0° , equal to the theoretical value.

Table 2. The edge lengths (Å) and bond angles ($^{\circ}$) of the vanadium coordination polyhedron (not designated in Fig. 1)

Distances and angles involving the point *M* bisecting the N(1)–N(3) distance are also given.

E.s.d.'s of the lengths are 0.003 Å, and of the angles 0.1° .

O(1)–O(2)	2.643		
O(1)–O(3)	2.821	O(1)–V–O(3)	104.6
O(1)–N(1)	2.811	O(1)–V–N(1)	98.2
O(1)–N(3)	3.231	O(1)–V–N(3)	118.1
O(2)–O(3)	2.749	O(2)–V–O(3)	100.4
O(2)–N(1)	2.748		
O(2)–N(3)	3.445	O(2)–V–N(3)	131.9
O(3)–N(1)	3.853	O(3)–V–N(1)	146.4
O(3)–N(3)	2.530		
N(1)–N(3)	2.457		
O(1)– <i>M</i>	2.768	O(1)–V– <i>M</i>	112.3
O(2)– <i>M</i>	2.864	O(2)–V– <i>M</i>	117.9
O(3)– <i>M</i>	3.019	O(3)–V– <i>M</i>	111.0

The VO₂ group takes a bent configuration with an O–V–O angle of $109.3(1)^{\circ}$ and V–O lengths of $1.615(2)$ and $1.625(2)$ Å. The VO₂ group with similar stereochemical parameters exists in the three V^v octahedral complexes: (NH₄)₃[VO₂(ox)₃].2H₂O (Scheidt, Tsai & Hoard, 1971), NH₄[VO₂(edtaH₂)].3H₂O (Scheidt, Collins & Hoard, 1971), and Na₃[VO₂(edta)].4H₂O (Scheidt, Countryman & Hoard, 1971). The six V–O bonds in these complexes range from 1.623 to 1.657 Å (average 1.643 Å) and the three bond angles from 103.8 to 107.1° (average 106.0°). The structure of the VO₂–par chelate strongly supports the considerations that the VO₂ group prefers a bent configuration and displays little variation in either bond angle or bond lengths in different environments. The bent VO₂ group is indicated also by the IR spectrum of the complex, which exhibits three bands associated with the VO₂ group at 940 , 845 and 410 cm⁻¹ assigned by analogy with the previously studied metal (*d*⁰)-dioxo complexes as $\nu_s(\text{VO}_2)$, $\nu_{as}(\text{VO}_2)$ and $\delta(\text{VO}_2)$ (Griffith & Wickins, 1968).

Four principal modes of coordination of azo compounds to transition metals have been structurally characterized (Little & Doedens, 1972). In the vanadium–par complex a very common mode of azo-ligand coordination is observed, through a single N atom of the azo group. The same mode and type of chelation is observed in the metal complexes with similar terdentate azo-ligands: 1-(2-pyridylazo)-2-naphthol (pan) and 1-(2-thiazolylazo)-2-naphthol (tan) (Table 4). These complexes are planar or nearly planar. The vanadium–par chelate is roughly planar, with maximum deviations of ± 0.28 Å. The displacement of atoms from the planes and the angles between these planes are given in Table 3. The dihedral angle C(29)–

Table 3. *Least-squares planes*

A, B, C, D: the phenyl-ring planes; *E*: the pyridine-ring plane; *F, G*: the five-membered chelate rings; *H*: the resorcinol ring; *I*: the plane through V and par anion; *J*: basal plane of the tetragonal pyramid.

(a) Equations of the least-squares planes in the form $PX + QY + RZ = S$

	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>		<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
<i>A</i>	-7.9837	8.8935	-1.1619	-2.8273	<i>F</i>	3.4847	14.4157	-9.0644	2.0070
<i>B</i>	-0.8137	-9.2754	15.0795	0.8163	<i>G</i>	3.8681	12.9586	-10.5585	0.9033
<i>C</i>	7.7768	9.9309	-1.0852	9.4128	<i>H</i>	3.5782	12.5195	-11.3714	-0.0071
<i>D</i>	0.7190	10.2912	14.2224	9.2562	<i>I</i>	3.6296	13.6840	-9.9339	1.1469
<i>E</i>	2.9954	14.7217	-9.1641	1.5693	<i>J</i>	0.6810	14.5573	-10.5796	-1.7873

(b) Deviations (in $\text{Å} \times 10^3$) of the cation atoms from the least-squares planes; atoms used in the calculation of the planes are denoted by asterisks

<i>A</i>		<i>B</i>		<i>C</i>		<i>D</i>	
C(1)*	7 (2)	C(7)*	-13 (5)	C(13)*	-2 (2)	C(19)*	2 (4)
C(2)*	-8 (2)	C(8)*	12 (5)	C(14)*	1 (3)	C(20)*	5 (5)
C(3)*	2 (3)	C(9)*	0 (6)	C(15)*	-2 (3)	C(21)*	-7 (5)
C(4)*	4 (3)	C(10)*	-10 (6)	C(16)*	2 (3)	C(22)*	1 (5)
C(5)*	-5 (3)	C(11)*	9 (6)	C(17)*	-3 (3)	C(23)*	6 (6)
C(6)*	0 (2)	C(12)*	3 (5)	C(18)*	3 (3)	C(24)*	-8 (6)
P	-109 (1)	P	-163 (1)	P	59 (1)	P	8 (1)
H(2)	27 (25)	H(8)	52 (51)	H(14)	-7 (25)	H(20)	10 (46)
H(3)	-26 (26)	H(9)	-19 (56)	H(15)	45 (29)	H(21)	9 (46)
H(4)	-13 (28)	H(10)	-27 (57)	H(16)	39 (29)	H(22)	18 (52)
H(5)	-32 (26)	H(11)	73 (51)	H(17)	-15 (36)	H(23)	-74 (55)
H(6)	-23 (23)	H(12)	20 (48)	H(18)	69 (27)	H(24)	-25 (47)

(c) Deviations (in $\text{Å} \times 10^3$) of the anion atoms from the least-squares planes and angles between selected planes; deviations of the atoms used in the calculation of the planes are denoted by asterisks

	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>	<i>J</i>
N(1)	10* (3)	-42* (3)	-284 (3)	-407 (3)	12* (3)	207* (3)
C(25)	-9* (4)	-120 (4)	-508 (4)	-645 (5)	-139* (5)	
C(26)	0* (4)	-101 (5)	-633 (5)	-849 (5)	-202* (5)	
C(27)	7* (4)	-21 (5)	-550 (5)	-835 (5)	-131* (5)	
C(28)	-6* (4)	26 (4)	-357 (5)	-629 (5)	-12* (4)	
C(29)	-3* (4)	17* (4)	-221 (4)	-411 (4)	62* (4)	
H(25)	34 (40)					
H(26)	95 (43)					
H(27)	-80 (45)					
H(28)	-88 (39)					
V	106 (1)	41* (1)	18* (1)	14 (1)	219* (1)	546 (1)
N(2)	-39 (3)	40* (3)	-51 (3)	-227 (3)	157* (3)	
N(3)	-110 (3)	-57* (3)	-32* (3)	-125 (3)	129* (3)	-228* (3)
O(1)	1599 (3)	1498 (3)	1442 (3)	1456 (3)	1667 (3)	2146 (3)
O(2)	-971 (3)	-1103 (3)	-1166 (3)	-1123 (3)	-939 (3)	-180* (3)
O(3)	-204 (4)	-221 (4)	-9* (4)	57 (5)	80* (5)	201* (5)
C(30)	-246 (4)	-148 (4)	33* (4)	-27* (4)	118* (4)	
C(31)	-318 (4)	-139 (4)	113 (5)	9* (5)	153* (5)	
C(32)	-553 (5)	-339 (5)	74 (5)	14* (5)	37* (5)	
C(33)	-747 (4)	-572 (4)	-52 (4)	-19* (4)	-130* (4)	
C(34)	-617 (4)	-523 (4)	-74 (4)	1* (4)	-108* (4)	
C(35)	-352 (4)	-296 (4)	-10* (4)	22* (4)	35* (4)	
O(4)	-1009 (3)	-798 (3)	-128 (3)	-57 (3)	-279* (3)	
H(31)				-36 (46)		
H(32)				14 (44)		
H(34)				-2 (40)		

Selected interplanar angles: (*EF*) 3.2; (*FG*) 7.0; (*GH*) 3.6; (*EH*) 10.4; (*EI*) 5.5; (*FI*) 3.7; (*GI*) 3.3; (*HI*) 6.0°.

N(2)—N(3)—C(30) is 175.6 (2)°. A deviation of C atoms from their least-squares plane reveals appreciable distortion of the resorcinol ring. Moreover, a difference in length between the four longer (average

1.445 Å) and two shorter C—C bonds (average 1.344 Å), along with a very short C(33)—O(4) length of 1.249 Å (close to a quinoid C=O length of 1.22 Å), indicates a structure with a more pronounced quinoid

Table 4. *The characteristic bond lengths (Å) involving the azo group in the pan, par, tan complexes and the Htan molecule*

C_p and C_h are C atoms from the phenolic and heterocyclic ring, respectively; the azo N atoms attached to them are designated as N_p and N_h , respectively.

	C_p-N_p	N_p-N_h	N_h-C_h
(a) [Cu(H ₂ O)(pan)] ⁺	1.39 (1)	1.27 (1)	1.43 (1)
(b) [PdCl(tan)]	1.34 (3)	1.39 (3)	1.34 (3)
(c) [Ni(tan) ₂]	1.40 (6)	1.26 (6)	1.47 (6)
(d) [Cu(tan)(H ₂ O) ₂] ⁺	1.36 (3)	1.27 (3)	1.40 (3)
(e) [Fe(tan) ₂]	1.40 (2)	1.31 (2)	1.39 (3)
(f) [Co(tan) ₂]	1.347 (8)	1.307 (7)	1.377 (8)
	1.350 (8)	1.294 (7)	1.369 (9)
(g) Htan	1.371 (7)	1.278 (6)	1.382 (7)
	1.359 (7)	1.306 (6)	1.378 (7)
(h) [VO ₂ (par)] ⁻	1.325 (4)	1.323 (3)	1.382 (4)

(a) Ooi, Carter & Fernando (1967), (b) Kurahashi (1974a), (c) Kurahashi (1974b), (d) Kurahashi & Kawase (1976a), (e) Kurahashi & Kawase (1976b), (f) Kurahashi (1976b), (g) Kurahashi (1976a), (h) this work.

character of the resorcinol ring in coordinated par. A non-aromatic ring is also indicated by ¹H NMR spectra of the complex. The N—N (1.323 Å) and the adjacent C—N lengths are all between single- and double-bond lengths indicating that the azo group is involved in resonance inside the VO₂—par chelate. A shorter C—N length with the resorcinol ring (1.325 Å) than that with the pyridine ring (1.362 Å) may indicate that the pyridine ring is less involved in the resonance. A strained structure of the chelate rings resulting from the steric conditions for complex formation, evident from some distorted angles, may influence both the resonance and the bond lengths.

A comparison of the complexes listed in Table 4 reveals a varying degree of the azo character of N—N bonds (presuming 1.24 Å for a standard azo-bond length). A number of factors such as electron-withdrawing powers of the metal, resonance possibility involving the ligand and chelate rings, steric requirements for chelate formation, the nature of other ligands in mixed complexes and different coordination polyhedra all may have a certain influence on the character of the azo bond. It seems that the double-bond character of the azo group is best preserved in the Cu (1.27 Å) and Ni (1.26 Å) chelates. A very long N—N length exists in [PdCl(tan)] (1.39 Å). Its molecular plane coincides with the crystallographic mirror plane.

Kurahashi (1976a) proposed a mechanism of metal-tan chelate formation through an azo but not hydrazone tautomer form.

According to the visible, IR and ¹H NMR spectra, undissociated par ligand (H₂par) exists in the solid state and in solution predominantly in the azophenol form.

This is in agreement with results reported for a number of arylazophenols.

When 4-(2-pyridylazo)resorcinol reacts with V under optimal conditions for [VO₂(par)]⁻ chelate formation (pH 5–6) both undissociated H₂par and anionic Hpar⁻ are present in solution in approximately equal amounts. It is likely that the reactive species are VO₂⁺ and Hpar⁻ ions although the reaction with H₂par also leads to the same complex. The proton from the *p*-hydroxy group may dissociate during the formation of the complex as a consequence of the acid-strengthening effect of the metal ion, observed in several metal—par chelates (Corsini, Fernando & Freiser, 1963).

The Hpar⁻ ion, formed by dissociation of the *p*-hydroxy group, is expected to stabilize by resonance in a conjugated system leading to a structure similar to that of the *p*-quinone hydrazone tautomer of H₂par (Hniličková & Sommer, 1961; Savvin, Grubov, Lebedev & Lihonina, 1971). The decrease of aromatic character of the resorcinol ring in the Hpar⁻ ion is indicated by the up-field shifts of proton signals in the NMR spectra of the sodium salt of the Hpar⁻ ion, with respect to the azophenol form of the H₂par molecule (Table 5). The analogous chemical shifts observed in the NMR spectra of the vanadium—par complex suggest a structure with a quinoid character of the coordinated ligand, which is in agreement with the X-ray results. Some down-field shifts of proton signals in the resorcinol ring, compared with the uncoordinated Hpar⁻ ion, are probably partly due to the lowering of the electron density caused by the electron-withdrawing effect of V.

Table 5. ¹H NMR chemical shifts (δ) relative to Me₄Si

Spectra were taken in CD₃SOCD₃ at room temperature.

	Chemical shifts (δ)						
	H ₂₅	H ₂₇	H ₂₈	H ₃₁	H ₂₆	H ₃₂	H ₃₄
H ₂ par	8.05	7.99	7.82	7.60	7.40	6.53	6.28
NaHpar	8.22	7.74	7.38	6.67	6.90	5.95	5.10
[Ph ₄ P][VO ₂ par]	Hidden by phosphonium protons		7.12	7.43	6.74	6.02	5.28

Table 6. *Ranges of bond lengths (Å) and angles (°) in the tetraphenylphosphonium ion with the corresponding mean values*

	Range	Mean
P—C	1.787 (3)–1.794 (2)	1.791 (3)
C—C	1.370 (4)–1.401 (4)	1.385 (4)
C—H	0.90 (3)–1.06 (3)	0.98 (3)
C—P—C	107.3 (1)–112.5 (1)	109.5 (1)
P—C—C	117.7 (2)–121.9 (2)	120.0 (2)
C—C—C	118.5 (2)–120.9 (3)	120.0 (3)
C—C—H	116 (2)–123 (2)	120 (2)

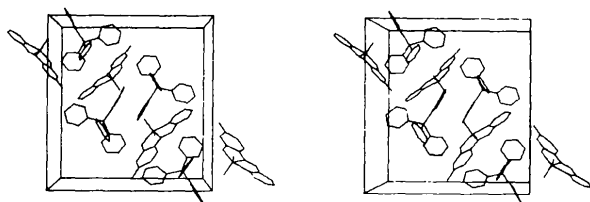


Fig. 3. A stereoview along *a* illustrating the packing of cations and anions in the unit cell. H atoms have been omitted. Drawings were made with the program POP1 (van de Waal, 1976).

Table 7. Possible hydrogen bonding

C_d is the hydrogen-donor C atom, O_a the hydrogen-acceptor O atom.

C_d	H	O_a	$C_d \cdots O_a$ (Å)	$H \cdots O_a$ (Å)	$C_d-H \cdots O_a$ (°)
C(2)	H(2)	O(2)*	3.180 (3)	2.36 (3)	139 (2)
C(4)	H(4)	O(4)*	3.453 (4)	2.55 (3)	151 (2)
C(6)	H(6)	O(1)	3.456 (3)	2.53 (2)	159 (2)

* Symmetry operations to be applied are:
on O(2) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; on O(4) $-1 + x, y, z$.

The bond lengths and angles in the tetraphenylphosphonium ion (Fig. 2, Table 6) are in good agreement with published values (Textor, Dubler & Oswald, 1974; Søtofte, 1976; Lazarini, 1977). The phenyl rings are planar to within ± 0.013 Å (Table 3). The angle between the mean planes through C(4), C(1), P, C(13), C(16) and C(10), C(7), P, C(19), C(22) is 89.5° .

The packing of tetraphenylphosphonium cations and VO_2 -par anions is illustrated in Fig. 3. All shorter intermolecular distances are consistent with normal van der Waals distances. Only three C—H \cdots O contacts (Table 7) may involve weak hydrogen bonding, especially the C(2)—H(2) \cdots O(2) contact of 3.180 Å and the H(2) \cdots O(2) separation of 2.36 Å. The remaining two contacts with H \cdots O separations of 2.55 and 2.53 Å are close to van der Waals contacts.

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