Fig. 2. Molecular packing and H-bonding scheme in the crystal structure of sodium D-gluconate. Roman numerals are the same as in Table 2(*b*).

The Na⁺ ion is coordinated to six O atoms belonging to six different gluconate anions. O(3) does not participate in the Na coordination. The polyhedron of the six O atoms is a distorted octahedron with the Na···O distances ranging from 2·340 (2) to 2·540 (2) Å.

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Structure of Tetraphenylphosphonium Dioxo[4-(1,3-thiazol-2-ylazo)resorcinolato]vanadate(V) Monohydrate, [P(C₆H₅)₄][VO₂(C₉H₅N₃O₂S)].H₂O

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Abstract. $M_r = 659·57$, triclinic, $P\bar{1}$, $a = 11·363$ (3), $b = 14·932$ (5), $c = 9·273$ (3) Å, $\alpha = 96·30$ (2), $\beta = 107·10$ (3), $\gamma = 91·65$ (1)°, $V = 1491·7$ (8) Å³, $Z = 2$, $D_m = 1·46$, $D_x = 1·468$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu = 4·355$ mm⁻¹, $F(000) = 680$, $T = 293$ K, final $R = 0·036$ for 4328 observed reflections. The 4-(1,3-thiazol-2-ylazo)resorcinolato anion (tar) acts as a terdentate ligand complexing V through the phenolic O atom, the azo N adjacent to the resorcinol ring, and the thiazolyl N atom, thus forming two five-membered chelate rings. Two oxo O atoms complete the pentagonal V coordination sphere with an O—V—O angle of 109·1 (1)° and V—O bond lengths of 1·613 (2) and 1·622 (3) Å. A resonance effect through the azo group is evident from the lengthened azo N—N bond of 1·343 (3) Å and shortened neighbouring N—C bonds of 1·318 (4) and 1·355 (4) Å.

Introduction. The thiazolylazophenols belong to a relatively large group of heterocyclic azo dyes with a wide range of applications. Heterocyclic *o*-hydroxy compounds have been used in analytical chemistry as spectrophotometric and extraction-spectrophotometric reagents for metal ions in aqueous and organic solutions and also as metallochromic indicators. As thiazolylazophenols are prepared more easily than the analogous pyridylazophenols, a large number of derivatives have been prepared and investigated for analytical purposes, but few have found extensive practical analytical application (Hovind, 1975).

4-(1,3-Thiazol-2-ylazo)resorcinol (H₂tar) is the most frequently used spectrophotometric reagent of the thiazolylazophenol class of azo dyes. It appears to be similar in character to the reagent 4-(2-pyridylazo)-resorcinol (H₂par). Differences and similarities between

coordinating tendencies of these two reagents were revealed in terms of the proton displacement constant and the acid dissociation constant of the metal complexes (Stanley & Cheney, 1966). In general H_2par forms slightly more stable complexes than H_2tar, and H_2tar complexes are more acidic than those of H_2par. There is some evidence that both reagents act as terdentate ligands toward bivalent metal ions. The terdentate coordination of par to V^V was confirmed by X-ray structure analysis of the $[Ph_4P][VO_2par]$ complex (Galešić & Široki, 1979). Recently, complementary to the study of extraction behaviour, the crystalline V^V–tar complexes have been prepared and characterized (Široki, Marić & Štefanac, 1981). In the present work the structure of the complex $[Ph_4P][VO_2tar].H_2O$ has been investigated and correlated with the structure of the par complex. A preliminary X-ray investigation has been reported recently (Galešić & Široki, 1982). No other structure studies on tar complexes have been published so far.

Table 1. *Fractional positional parameters* ($\times 10^4$; $\times 10^5$ *for* V, S *and* P), *and equivalent isotropic temperature factors* ($\times 10^2$) *for non-*H *atoms*

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
V	60606 (5)	35162 (3)	51635 (6)	2·99 (2)
S	81716 (7)	56088 (6)	90127 (10)	4·67 (3)
P	74959 (7)	90148 (5)	102710 (8)	2·85 (2)
O(1)	6592 (2)	2600 (1)	5802 (3)	4·9 (1)
O(2)	6484 (2)	3656 (2)	3675 (2)	4·7 (1)
O(3)	4304 (2)	3212 (2)	4220 (3)	4·5 (1)
O(4)	355 (2)	3260 (2)	4942 (3)	6·1 (1)
O$_w$	8407 (2)	3655 (2)	2324 (3)	6·4 (1)
N(1)	7360 (2)	4453 (2)	6634 (3)	3·3 (1)
N(2)	5841 (2)	4845 (2)	7850 (3)	3·6 (1)
N(3)	5192 (2)	4273 (2)	6638 (3)	3·0 (1)
C(1)	8830 (3)	8368 (2)	10506 (3)	3·2 (1)
C(2)	9476 (3)	8308 (2)	9439 (4)	3·9 (1)
C(3)	10489 (3)	7779 (2)	9642 (4)	4·9 (1)
C(4)	10850 (3)	7323 (2)	10900 (5)	5·1 (1)
C(5)	10211 (3)	7384 (2)	11966 (4)	4·7 (1)
C(6)	9194 (3)	7893 (2)	11775 (4)	3·9 (1)
C(7)	6282 (3)	8291 (2)	10461 (3)	3·1 (1)
C(8)	5565 (3)	8554 (2)	11410 (4)	4·0 (1)
C(9)	4628 (3)	7960 (3)	11491 (4)	4·9 (1)
C(10)	4396 (3)	7120 (2)	10640 (4)	4·7 (1)
C(11)	5115 (3)	6853 (2)	9724 (4)	4·4 (1)
C(12)	6061 (3)	7430 (2)	9629 (4)	3·8 (1)
C(13)	7101 (3)	9390 (2)	8422 (3)	3·2 (1)
C(14)	7644 (3)	10201 (2)	8245 (4)	4·5 (1)
C(15)	7436 (4)	10472 (2)	6805 (4)	5·3 (1)
C(16)	6709 (4)	9922 (3)	5573 (4)	6·8 (2)
C(17)	6166 (5)	9117 (3)	5727 (4)	7·6 (2)
C(18)	6350 (4)	8844 (2)	7165 (4)	5·1 (1)
C(19)	7821 (3)	9999 (2)	11648 (3)	3·2 (1)
C(20)	6922 (3)	10629 (2)	11570 (4)	4·0 (1)
C(21)	7156 (4)	11406 (2)	12596 (4)	4·8 (1)
C(22)	8289 (4)	11568 (2)	13690 (4)	5·2 (1)
C(23)	9190 (4)	10963 (2)	13758 (4)	5·3 (1)
C(24)	8961 (3)	10169 (2)	12749 (4)	4·2 (1)
C(25)	8585 (3)	4672 (2)	6775 (4)	3·8 (1)
C(26)	9166 (3)	5270 (2)	7989 (4)	4·4 (1)
C(27)	7003 (3)	4908 (2)	7740 (3)	3·3 (1)
C(28)	4008 (3)	4058 (2)	6374 (4)	3·0 (1)
C(29)	3225 (3)	4360 (2)	7263 (4)	3·8 (1)
C(30)	2028 (3)	4085 (2)	6789 (4)	4·2 (1)
C(31)	1488 (3)	3485 (2)	5359 (4)	4·2 (1)
C(32)	2288 (3)	3173 (2)	4493 (4)	4·2 (1)
C(33)	3508 (3)	3450 (2)	4966 (3)	3·4 (1)

Experimental. Dark-red crystals obtained according to the procedure described by Široki, Marić & Štefanac (1981). D_m by flotation in a mixture of CCl_4 and benzene. Philips PW 1100 four-circle diffractometer, θ–2θ scanning technique, scan range 1·20°, scan rate 0·04° s^{-1}. Prismatic crystal 0·18 × 0·08 × 0·53 mm, crystal faces $\pm(100)$, $\pm(010)$, $\pm(001)$. Unit cell: least-squares analysis of 21 reflections, 2θ from 18 to 33°. No systematically absent reflections; structure determination confirmed $P\bar{1}$. 4798 reflections scanned within the hemisphere $\pm h$, $\pm k$, l (h ± 13; k 17, -18; l 11), sin $\theta/\lambda \le 0·61$ Å^{-1}; 4328 unique with $I > 3\sigma(I)$ classified as observed. Three standard reflections (04$\bar{1}$, 301, $\bar{1}$30) measured after each group of about 100 measurements showed an averaged variation of 0·6 (2)%. Corrections applied for Lorentz and polarization effects and for absorption; transmission factors 0·38 to 0·72. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Of 44 non-H atoms 38 were obtained from the E map calculated with the 422 largest E values ($E \ge 1·59$). Subsequent calculations performed mainly with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Remaining non-H atoms located from a subsequent Fourier map and all H atoms from both theoretical calculations and a difference map. Block-diagonal least-squares refinement on F with anisotropic thermal parameters for non-H and isotropic for H gave $R = 0·036$. Unit weights; $S = 0·96$. $(\Delta/\sigma)_{max} = 0·2$, $(\Delta/\sigma)_{mean} = 0·1$. Final difference map revealed no residuals greater than 0·25 e Å^{-3}. Scattering factors of Cromer & Mann (1968) for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). Thermogravimetric analysis performed on a Cahn RG electrobalance. All calculations performed on a Univac 1110 computer at the University Computing Centre in Zagreb.

Discussion. Final atomic parameters are given in Table 1.*

The crystalline V^V–tar complexes have been characterized by elemental analyses, UV/visible, IR and ^{1}H NMR spectra, magnetic susceptibility, TGA and DCA data (Široki, Marić & Štefanac, 1981). The hydrated compounds were found to contain 1–2 molecules of water, some of which, unlike V–par complexes (Široki & Djordjević, 1977), is released just before the melting point is reached (503 K). The results of the

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39009 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

thermogravimetric analyses reinvestigated during the structure determination showed a weight loss of 2·9 (6)% between 492 and 510 K, corresponding to 1·1 (2) molecules of water. Unfortunately, the reproducibility of the determination of the temperature at which complete dehydration occurred was difficult due to the nearness of the decomposition point (513 K).

The monohydrate crystals were selected for structure investigation. The structural analysis of [Ph₄P]-[VO₂tar].H₂O was carried out in order to confirm the mode of coordination of the tar ligand, which in relation to par contains additionally the thiazole S as potential donor atom. The structure analysis verifies the terdentate coordination of tar, analogous to that of the par ligand: the phenolic O in the *ortho* position, the azo N atom adjacent to the resorcinol ring and the thiazolyl N atom being coordinated to the V atom, thus giving two five-membered chelate rings. Fig. 1 shows a perspective view of the dioxo(tar)vanadate(V) anion with the atomic numbering. Intramolecular bond lengths and angles listed in Table 2 show an obvious similarity with analogous values for dioxo(par)vanadate(V) (Galešić & Široki, 1979). The thiazole S atom does not coordinate to metal as expected from chemical and spectral evidence (Široki, Marić & Štefanac, 1981, and references therein). The same had been found true for the complexes of 1-(1,3-thiazol-2-ylazo)-2-naphthol (Kurahashi, 1976). The coordination number and geometry around V are very close to those of the par complex. The VO₂ group preserves very nearly the same stereochemical parameters. The water molecule does not enter the ligand sphere, but it is hydrogen bonded to the basal vanadyl O and to the *para* phenolic O of the adjacent complex anion. The coordination sphere of V in the tar, as well as in the par complex, can be described as a distorted tetragonal pyramid with the O(1) oxo oxygen at the apical position. The deviations of the atoms from the basal plane, O(2) 0·124 (3), N(1) −0·141 (3), N(3) 0·154 (2) and O(3) −0·138 (3) Å, indicate a tetrahedral distortion smaller than in the par complex. The angle between the O(1)−V bond and the normal to the basal plane is 4·7 (1)°. The V atom is 0·522 (1) Å above the plane of the basal atoms,

compared with the value of 0·546 (1) Å for the par complex. As expected a bent configuration of the VO₂ group is confirmed by the O−V−O angle of 109·1 (1)°, which is close to the value reported for the par complex [109·3 (1)°].

The V−tar chelate atoms deviate within ±0·237 (3) Å and the atoms of the tar ligand alone within ±0·064 (4) Å from their mean planes. The thiazolyl and resorcinol rings are planar within ±0·007 (3) and ±0·011 (4) Å respectively. The chelate ring adjacent to the thiazolyl ring deviates from

Table 2. *Intramolecular bond lengths* (Å) *and angles* (°) *of non*-H *atoms*

The numbering of cation C atoms is from C(1) to C(24) and the numbering of anion atoms is shown in Fig. 1.

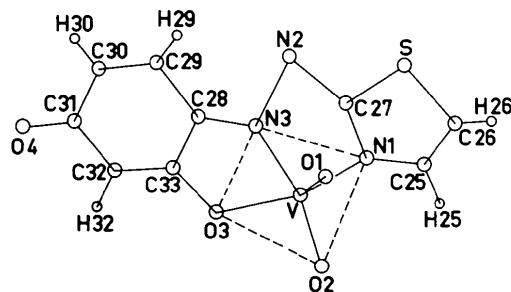|			
V−O(1)	1·613 (2)	C(1)−C(2)	1·392 (5)
V−O(2)	1·622 (3)	C(1)−C(6)	1·404 (5)
V−O(3)	1·947 (2)	C(2)−C(3)	1·393 (5)
V−N(1)	2·067 (2)	C(3)−C(4)	1·379 (6)
V−N(3)	2·154 (3)	C(4)−C(5)	1·385 (6)
S−C(26)	1·730 (4)	C(5)−C(6)	1·379 (5)
S−C(27)	1·727 (3)	C(7)−C(8)	1·399 (5)
O(3)−C(33)	1·324 (4)	C(7)−C(12)	1·399 (4)
O(4)−C(31)	1·254 (4)	C(8)−C(9)	1·391 (5)
N(1)−C(25)	1·386 (4)	C(9)−C(10)	1·381 (5)
N(1)−C(27)	1·336 (4)	C(10)−C(11)	1·379 (6)
N(2)−N(3)	1·343 (3)	C(11)−C(12)	1·388 (5)
N(2)−C(27)	1·355 (4)	C(13)−C(14)	1·391 (5)
N(3)−C(28)	1·318 (4)	C(13)−C(18)	1·385 (4)
C(25)−C(26)	1·344 (4)	C(14)−C(15)	1·393 (5)
C(28)−C(29)	1·431 (5)	C(15)−C(16)	1·365 (5)
C(28)−C(33)	1·458 (4)	C(16)−C(17)	1·376 (7)
C(29)−C(30)	1·337 (4)	C(17)−C(18)	1·396 (6)
C(30)−C(31)	1·472 (4)	C(19)−C(20)	1·400 (5)
C(31)−C(32)	1·435 (5)	C(19)−C(24)	1·390 (4)
C(32)−C(33)	1·362 (4)	C(20)−C(21)	1·383 (4)
P−C(1)	1·793 (3)	C(21)−C(22)	1·380 (5)
P−C(7)	1·789 (3)	C(22)−C(23)	1·377 (6)
P−C(13)	1·797 (3)	C(23)−C(24)	1·394 (5)
P−C(19)	1·791 (3)		
O(1)−V−O(2)	109·1 (1)	C(1)−P−C(13)	108·7 (2)
O(1)−V−O(3)	104·2 (1)	C(1)−P−C(19)	110·6 (1)
O(1)−V−N(1)	99·8 (1)	C(7)−P−C(13)	111·3 (1)
O(1)−V−N(3)	112·5 (1)	C(7)−P−C(19)	111·7 (2)
O(2)−V−O(3)	100·3 (1)	C(13)−P−C(19)	107·5 (1)
O(2)−V−N(1)	95·5 (1)	P−C(1)−C(2)	121·4 (2)
O(2)−V−N(3)	137·9 (1)	P−C(1)−C(6)	118·5 (3)
O(3)−V−N(1)	144·9 (1)	C(2)−C(1)−C(6)	120·1 (3)
O(3)−V−N(3)	75·6 (1)	C(1)−C(2)−C(3)	119·7 (3)
N(1)−V−N(3)	71·6 (1)	C(2)−C(3)−C(4)	119·9 (4)
C(26)−S−C(27)	89·8 (2)	C(3)−C(4)−C(5)	120·5 (3)
V−O(3)−C(33)	120·0 (2)	C(4)−C(5)−C(6)	120·5 (3)
V−N(1)−C(25)	132·5 (2)	C(1)−C(6)−C(5)	119·3 (3)
V−N(1)−C(27)	115·7 (2)	P−C(7)−C(8)	122·4 (2)
C(25)−N(1)−C(27)	111·7 (2)	P−C(7)−C(12)	118·0 (3)
N(3)−N(2)−C(27)	105·6 (3)	C(8)−C(7)−C(12)	119·6 (3)
V−N(3)−N(2)	122·1 (2)	C(7)−C(8)−C(9)	119·3 (3)
V−N(3)−C(28)	115·3 (2)	C(8)−C(9)−C(10)	120·7 (4)
N(2)−N(3)−C(28)	122·2 (3)	C(9)−C(10)−C(11)	120·1 (3)
N(1)−C(25)−C(26)	114·6 (3)	C(10)−C(11)−C(12)	120·3 (3)
S−C(26)−C(25)	110·9 (3)	C(7)−C(12)−C(11)	119·9 (3)
S−C(27)−N(1)	113·1 (2)	P−C(13)−C(14)	119·1 (2)
S−C(27)−N(2)	122·8 (2)	P−C(13)−C(18)	120·5 (3)
N(1)−C(27)−N(2)	124·1 (2)	C(14)−C(13)−C(18)	120·2 (3)
N(3)−C(28)−C(29)	128·0 (2)	C(13)−C(14)−C(15)	120·4 (3)
N(3)−C(28)−C(33)	111·6 (3)	C(14)−C(15)−C(16)	118·9 (4)
C(29)−C(28)−C(33)	120·3 (3)	C(15)−C(16)−C(17)	121·5 (4)
C(28)−C(29)−C(30)	119·5 (3)	C(16)−C(17)−C(18)	120·2 (3)
C(29)−C(30)−C(31)	121·6 (3)	C(13)−C(18)−C(17)	118·9 (3)
O(4)−C(31)−C(30)	119·4 (3)	P−C(19)−C(20)	119·0 (2)
O(4)−C(31)−C(32)	122·3 (3)	P−C(19)−C(24)	121·5 (2)
C(30)−C(31)−C(32)	118·3 (3)	C(20)−C(19)−C(24)	119·4 (3)
C(31)−C(32)−C(33)	120·5 (3)	C(19)−C(20)−C(21)	120·4 (3)
O(3)−C(33)−C(28)	115·8 (2)	C(20)−C(21)−C(22)	119·8 (3)
O(3)−C(33)−C(32)	124·5 (3)	C(21)−C(22)−C(23)	120·3 (3)
C(28)−C(33)−C(32)	119·7 (3)	C(22)−C(23)−C(24)	120·5 (3)
C(1)−P−C(7)	107·1 (1)	C(19)−C(24)−C(23)	119·5 (3)

Fig. 1. A perspective view of the complex anion along **b** showing the atomic numbering. The basal plane of a tetragonal pyramid of the V polyhedron is outlined with dashed lines.
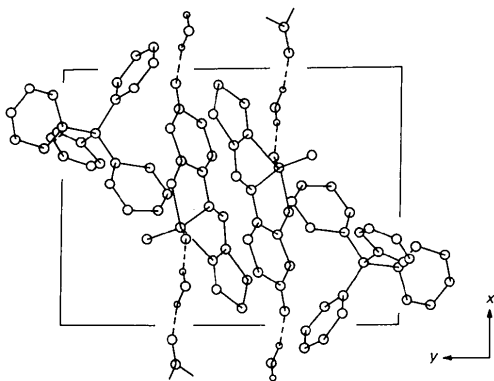
Fig. 2. A projection of the structure viewed along **c**. Dashed lines denote hydrogen bonds. Only the water H atoms are represented for reasons of clarity.

Table 3. *Geometry of the hydrogen bonds*

D	H	A	$D\cdots A$ (Å)	$D-H$ (Å)	$H\cdots A$ (Å)	$D-H\cdots A$ (°)
O_w	$H_w(1)$	$O(2)$	2·820 (4)	0·89 (6)	1·94 (5)	172 (4)
O_w	$H_w(2)$	$O(4^i)$	2·893 (4)	0·95 (5)	1·95 (5)	171 (5)

Symmetry code: (i) $1 + x, y, z$.

planarity within ± 0.065 (2) Å and that adjacent to the resorcinol ring within ± 0.076 (2) Å.

A quinoid character of the resorcinol ring, as expected from the ^{1}H NMR spectra, is indicated by the short C(31)—O(4) bond length of 1·254 (4) Å and four longer and two shorter C—C bond lengths with averages of 1·449 (20) and 1·350 (13) Å respectively.

The N—N bond length of 1·343 (3) Å is a little longer than the analogous value of 1·323 (3) Å for the par complex, indicating a weakening of the azo double-bond character in the tar complex. On the other hand, the two neighbouring C—N bond lengths in the tar complex are a little shorter than in the par complex, so that their sum remains nearly the same for both complexes within the limits of the estimated standard deviations.

The intramolecular geometry in the tetraphenylphosphonium ion does not show any unusual features. The phenyl rings are planar within ± 0.009 (4) Å. 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 86·0 (1)°. All C—H bond lengths fall within the range 0·88 (5) to 1·11 (4) Å.

The three-dimensional network of the structure (Fig. 2) is stabilized by the hydrogen bonds formed between crystal water molecules and basal oxo and quinoid resorcinol O atoms from different neighbouring complex anions. The geometry of the hydrogen bonding is given in Table 3.

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Structure of Tribromobis(triphenylphosphine oxide)thallium(III), [TlBr₃{OP(C₆H₅)₃}₂]

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Abstract. $M_r = 1000.7$, monoclinic, $P2_1/c$, $a = 14.85$ (1), $b = 14.60$ (1), $c = 17.37$ (2) Å, $\beta = 107.7$ (1)°, $Z = 4$, $D_x = 1.85$, $D_m = 1.712$ Mg m^{-3}, $V = 3587.1$ Å^3, λ(Mo $K\alpha$) = 0·7106 Å, $\mu = 7.7$ mm^{-1}, $F(000) = 1912$, room temperature, $R = 0.0542$, 2670 intensities. The unit cell contains discrete TlBr₃.2OPPh₃ molecules which have distorted trigonal-bipyramidal geometry.