

**Data collection**

Syntex P2 <sub>1</sub> diffractometer	$\theta_{\max} = 27.56^\circ$
$\omega$ -2 $\theta$ scans	$h = -20 \rightarrow 14$
Absorption correction: none	$k = -14 \rightarrow 12$
8427 measured reflections	$l = -22 \rightarrow 22$
3242 independent reflections	3 standard reflections
2808 reflections with $I > 4\sigma(I)$	every 100 reflections
$R_{\text{int}} = 0.053$	intensity decay: none

**Refinement**

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 1.0143P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\max} = -0.001$
$S = 1.241$	$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
3242 reflections	$\Delta\rho_{\min} = -1.08 \text{ e } \text{\AA}^{-3}$
133 parameters	Extinction correction: none
H-atom parameters constrained	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993a).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1009). Services for accessing these data are described at the back of the journal.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{eq}}$
Zr	0.36911 (2)	0.34704 (2)	0.22495 (2)	0.04290 (13)
Cl1	0.33405 (8)	0.16883 (8)	0.13446 (6)	0.0648 (2)
Cl2	0.37778 (8)	0.54499 (8)	0.29089 (6)	0.0694 (3)
Cl3	0.37036 (8)	0.23894 (9)	0.34475 (5)	0.0679 (3)
O	1/2	0.3391 (3)	1/4	0.0582 (8)
O1	0.3464 (2)	0.4559 (2)	0.11102 (13)	0.0548 (5)
O2	0.2110 (2)	0.3714 (3)	0.1764 (2)	0.0600 (6)
C1	0.3846 (3)	0.4195 (4)	0.0512 (2)	0.0630 (9)
C2	0.3866 (4)	0.5315 (5)	0.0054 (3)	0.089 (2)
C3	0.3144 (6)	0.6105 (6)	0.0131 (4)	0.125 (3)
C4	0.3109 (5)	0.5781 (5)	0.0910 (3)	0.107 (2)
C5	0.1605 (3)	0.4046 (5)	0.2271 (3)	0.0804 (12)
C6	0.0598 (4)	0.3944 (7)	0.1726 (5)	0.108 (2)
C7	0.0555 (4)	0.3818 (9)	0.0895 (4)	0.126 (3)
C8	0.1420 (4)	0.3377 (7)	0.0954 (3)	0.098 (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

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### [N,N'-Bis(5-methoxysalicylidene)-1,2-diphenyl-1,2-ethenediamine]-oxovanadium(IV)†

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**Abstract**

The title complex, [VO(C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>)], adopts a monomeric structure in the crystals, which are red due to the charge-transfer band from the conjugated  $\pi$ -system of the tetradentate Schiff base ligand. The geometry around the V<sup>IV</sup> atom is distorted square pyramidal. The V=O distance is 1.588 (3) Å, and the V atom is displaced by 0.57 (1) Å from the N<sub>2</sub>O<sub>2</sub> coordination plane towards the apical oxo ligand.

**Comment**

Upon heating at 483 K, the green powder of [VO(5-MeOsal-meso-stien)] [H<sub>2</sub>(5-MeOsal-meso-stien)

† Alternative name: {4,4'-dimethoxy-2,2'-[1,2-diphenylethene-1,2-diy]bis(nitrimethylidyne)}diphenolato-*O,N,N',O'*oxovanadium(IV).

Table 2. Selected geometric parameters ( $\text{\AA}$ , °)

Zr—O	1.9212 (10)	Zr—Cl3	2.4194 (13)
Zr—O1	2.243 (2)	Zr—Cl1	2.4506 (13)
Zr—O2	2.292 (3)	Zr—Cl2	2.4510 (14)
O—Zr—O1	90.05 (11)	O2—Zr—Cl1	85.68 (8)
O—Zr—O2	171.03 (8)	Cl3—Zr—Cl1	95.45 (5)
O1—Zr—O2	81.02 (11)	O—Zr—Cl2	94.66 (10)
O—Zr—Cl3	98.27 (9)	O1—Zr—Cl2	84.69 (7)
O1—Zr—Cl3	171.44 (7)	O2—Zr—Cl2	85.32 (8)
O2—Zr—Cl3	90.69 (9)	Cl3—Zr—Cl2	92.56 (5)
O—Zr—Cl1	93.01 (10)	Cl1—Zr—Cl2	168.00 (4)
O1—Zr—Cl1	86.09 (8)	Zr—O—Zr <sup>†</sup>	174.8 (2)

Symmetry code: (i) 1 - x, y,  $\frac{1}{2}$  - z.

H atoms were fixed at ideal positions with  $d(\text{C—H}) = 0.97 \text{ \AA}$  and with a common isotropic displacement parameter ( $U_{\text{iso}} = 0.15 \text{ \AA}^2$ ). All crystallographic calculations were carried using *SHELXL93* (Sheldrick, 1993a) and *SHELXTL-Plus* (Sheldrick, 1993b). The largest residue peak ( $1.08 \text{ e } \text{\AA}^{-3}$ ) lay close to the heavy Zr atom in the final cycle of refinement. The C7—C8 distance is clearly shorter than the normal  $\text{Csp}^3\text{—Csp}^3$  bond length; this may be due to the strong thermal motion of the C atoms in the THF molecule.

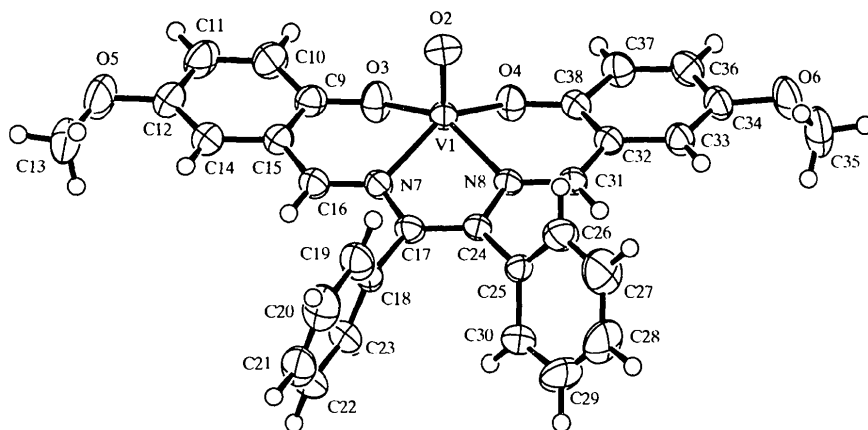
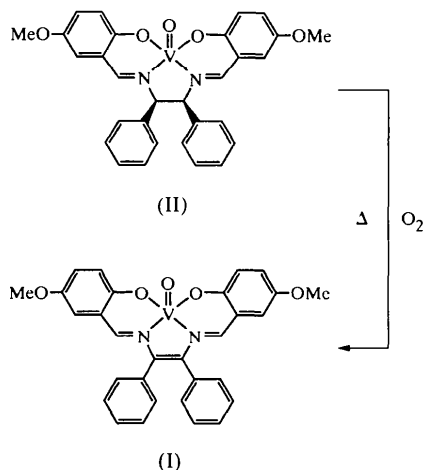


Fig. 1. ORTEPII (Johnson, 1976) drawing of (I) with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

is *N,N'*-bis(5-methoxysalicylidene)-(*RS,SR*)-1,2-diphenyl-1,2-ethanediamine], (II), was transformed into the red-brown powder of [VO(5-MeOsaltan)] [H<sub>2</sub>(5-MeOsaltan) is *N,N'*-bis(5-methoxysalicylidene)-1,2-diphenyl-1,2-ethanediamine], (I). The solid-state thermal reaction is a dehydrogenation of the stien ligand by O<sub>2</sub> in air. In our previous study (Hoshina *et al.*, 1998), the crystal structure of the red complex [VO(3-EtOsaltan)(H<sub>2</sub>O)]·0.5H<sub>2</sub>O·0.5CH<sub>3</sub>CN was determined, and a water molecule coordinating to the V atom at a distance of 2.406(3) Å was observed. We report here the crystal structure of the title red complex, (I).



Monomeric oxovanadium(IV) complexes are usually green. An orange or red colour of the solid indicates one of three possibilities: (a) a polynuclear linear chain structure (V=O···V=O···), as observed in [VO(salpn)] [H<sub>2</sub>salpn is *N,N'*-bis(salicylidene)propanediamine; Mathew *et al.*, 1970], (b) coordination of a solvent molecule, as in [VO(salpn)(DMSO)] (DMSO is dimethyl sulfoxide; Root *et al.*, 1993), or (c) a relatively

long conjugated  $\pi$ -system of the tetradentate Schiff base ligand, as in [VO(salphen)] [H<sub>2</sub>salphen is *N,N'*-bis(salicylidene)-*o*-phenylenediamine], which takes a five-coordinated mononuclear structure (Wang *et al.*, 1995). In cases (a) and (b), the energy levels of the *d* orbitals are affected by the coordination at the sixth position, *trans* to the oxo atom (Boucher *et al.*, 1968). The present work confirms that the red colour of (I) is due to case (c). The absorption spectra of an acetonitrile solution of (I) show a strong charge-transfer band, which covers the *d-d* transitions. The C=C bond distance in the ethenediamine moiety of the saltan ligand is 1.356(5) Å.

## Experimental

The preparation of (II) and the thermal dehydrogenation reaction which forms (I) have been reported previously by Hoshina *et al.* (1998). Red crystals of (I) were grown from acetonitrile solution.

### Crystal data

[VO(C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>)]

*M<sub>r</sub>* = 543.47

Triclinic

*P*1

*a* = 10.375(2) Å

*b* = 13.300(2) Å

*c* = 10.314(1) Å

$\alpha$  = 106.18(1)°

$\beta$  = 94.40(1)°

$\gamma$  = 71.86(1)°

*V* = 1298.7(4) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.390 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

### Data collection

Rigaku AFC-5R diffractometer

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25

reflections

$\theta$  = 14.2–14.7°

$\mu$  = 0.425 mm<sup>-1</sup>

*T* = 297 K

Prism

0.5 × 0.3 × 0.1 mm

Red

*R*<sub>int</sub> = 0.024

$\theta_{\text{max}}$  = 27.5°

$\theta/2\theta$  scans  $h = 0 \rightarrow 13$   
 Absorption correction:  $k = -17 \rightarrow 17$   
 $\psi$  scan (North *et al.*,  
 1968)  $l = -13 \rightarrow 13$   
 $T_{\min} = 0.967$ ,  $T_{\max} = 0.999$  3 standard reflections  
 6308 measured reflections every 100 reflections  
 5976 independent reflections intensity decay: none  
 3759 reflections with  
 $I > 2\sigma(I)$

#### Refinement

Refinement on  $F$   $w = 1/[\sigma^2(F_o) + 0.0019|F_o|^2]$   
 $R = 0.053$   $(\Delta/\sigma)_{\max} = 0.001$   
 $wR = 0.071$   $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$   
 $S = 1.10$   $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$   
 3956 reflections Extinction correction: none  
 343 parameters Scattering factors from  
 H-atom parameters not *International Tables for*  
 refined *Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

V1—O2	1.588 (3)	N7—C16	1.299 (4)
V1—O3	1.926 (3)	N7—C17	1.416 (4)
V1—O4	1.934 (2)	N8—C24	1.422 (4)
V1—N7	2.078 (3)	N8—C31	1.297 (4)
V1—N8	2.072 (3)	C17—C24	1.356 (5)
O2—V1—O3	108.1 (1)	O3—V1—N7	87.1 (1)
O2—V1—O4	109.2 (1)	O4—V1—N8	88.2 (1)
O2—V1—N7	105.5 (1)	N7—V1—N8	77.3 (1)
O2—V1—N8	103.6 (1)	N7—C17—C24	116.4 (3)
O3—V1—O4	88.4 (1)	N8—C24—C17	115.2 (3)

All H-atom positions were calculated geometrically.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1233). Services for accessing these data are described at the back of the journal.

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### Aqua(benzo-15-crown-5)lithium-hexa- $\mu$ -iodotetracopper-benzo-15-crown-5 (2/1/2), bis[bis(benzo-15-crown-5)caesium] hexa- $\mu$ -iodotetracopper and $\mu$ -aqua-bis[aqua(18-crown-6)sodium] hexa- $\mu$ -iodotetracopper†

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#### Abstract

The title compounds,  $[\text{Li}(\text{C}_{14}\text{H}_{20}\text{O}_5)(\text{H}_2\text{O})]_2[\text{Cu}_4\text{I}_6] \cdot 2\text{C}_{14}\text{H}_{20}\text{O}_5$ ,  $[\text{Cs}(\text{C}_{14}\text{H}_{20}\text{O}_5)_2]_2[\text{Cu}_4\text{I}_6]$  and  $[\text{Na}_2(\text{C}_{12}\text{H}_{24}\text{O}_6)_2(\text{H}_2\text{O})_3][\text{Cu}_4\text{I}_6]$ , respectively, all show similar  $[\text{Cu}_4\text{I}_6]^{2-}$  clusters disordered about a center of symmetry. The Cu atoms are three-coordinate, with an average Cu—I distance of 2.596 (3)  $\text{\AA}$ . Alkali-bound crown-ether groups serve as counter-ions. The three solid materials display identical emission in the visible when excited in the ultraviolet. Calculations of the atomic contributions to frontier orbitals show the highest occupied molecular orbital (HOMO) to be based primarily on contributions from four of the six I atoms and the lowest unoccupied molecular orbital (LUMO) to be primarily copper-based and involving contributions from the four Cu atoms.

#### Comment

Copper halide complexes adopt a wide variety of stoichiometries in the formation of neutral (Caulton *et al.*, 1990) and anionic clusters of diverse form (Jagner & Helgesson, 1991; Hu & Holt, 1994*a,b,c,d*; Nurtaeva & Holt, 1998*a,b*). Many of these solid-state complexes have been shown to emit in the visible range when excited in the ultraviolet (Rath & Holt, 1985; Rath *et al.*, 1985), however, quenching effects due to delocalized  $\pi$  systems in the accompanying cation may interfere with the observation of emission (Tompkins *et al.*, 1987; Hu *et al.*, 1995). We have prepared a series of copper iodide

† Systematic nomenclature: benzo-15-crown-5 is 2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-15,17,19-triene and 18-crown-6 is 1,4,7,10,13,16-hexaazacyclooctadecane.