Compartmental Ligands. Part 4.[1] The Crystal and Molecular Structures † of some Oxovanadium(IV) Complexes of Acyclic Ligands derived from Heptane-2,4,6-trione and α,ω-Alkanediamines

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Mononuclear oxovanadium(IV) complexes of acyclic Schiff bases derived from heptane-2,4,6-trione and α,ω-alkanediamines have been synthesised from the corresponding macrocyclic precursors. Three-dimensional *X*-ray crystal-structure analyses have been carried out on [6,12-dimethyl-7,11-diazaheptadeca-5,12-diene-2,4,14,16-tetraonato(2−)-$O^2O^4O^{14}O^{16}$]oxovanadium(IV)–chloroform (1/1), (4b; M = VO)·CHCl$_3$, and two forms of [6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(2−)-$O^2O^4O^{13}O^{15}$]oxovanadium(IV), (4a; M = VO). The last two forms gave evidence for co-crystallisation of the corresponding homobinuclear bis(oxovanadium) complex. Complex (4b; M = VO)·CHCl$_3$, has $Z = 2$ in a triclinic cell with space group $P\bar{1}$, and dimensions a = 10.966(5), b = 8.358(4), c = 15.226(8) Å, α = 92.36(8), β = 123.77(11), and γ = 102.16(10)°; R = 0.0385 for 2 985 reflections. Complex (4a; M = VO) has $Z = 4$ in a monoclinic unit cell with space group $P2_1/n$ and dimensions a = 9.230(3), b = 23.657(15), c = 8.177(6) Å, and β = 102.160(14)° (R = 0.0638 for 987 reflections), and has $Z = 2$ in a triclinic cell with space group $P\bar{1}$ and dimensions a = 8.459(6), b = 12.002(9), c = 8.789(7) Å, α = 80.140(7), β = 101.447(12), and γ = 93.946(7)° (R = 0.0545 for 1 598 reflections). The *X*-ray structure of the heterobinuclear complex [6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(4−)-$N^7N^{10}O^4O^{13}$; $O^2O^4O^{13}O^{15}$]-copper(II)oxovanadium(IV), (5a; M^1 = Cu, M^2 = VO), is also reported and has $Z = 4$ in a monoclinic cell with space group $P2_1/c$ and dimensions a = 8.325(20), b = 12.117(11), c = 18.105(18) Å, and β = 108.93(6)°; R = 0.0613 for 2 480 reflections. The crystal structures confirm the compartmental occupancies for the complexes and show that the Cu–V distance in (5a; M^1 = Cu, M^2 = VO) is 2.985 Å. A proposal is made for the mode of incorporation of the second oxovanadium into the mononuclear complex.

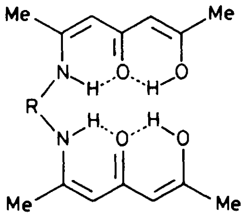
Recently there has been considerable interest shown in the design and synthesis of binucleating ligands.[2–4] Impetus for these studies has come from the potential application of metal complexes formed from such ligands to areas such as homogeneous catalysis, the study of magnetic interactions between metals held in close proximity, and the development of speculative models for dimetallic sites in metalloproteins.

We have previously reported the synthesis and properties of mononuclear, homobinuclear, and heterobinuclear complexes of potentially binucleating ligands derived from heptane-2,4,6-trione and α,ω-alkanediamines and collectively termed compartmental ligands.[1,5,6,‡]

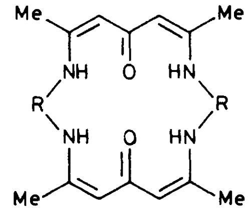
This paper reports the *X*-ray and molecular structures of the mononuclear oxovanadium(IV) complexes of the compartmental ligands (1a) and (1b), the first of which exists in two distinct crystalline forms dependent upon the synthetic pathway, and of the heterobinuclear complex of (1a) with Cu and VO. We also show the existence of a homobinuclear bis[oxovanadium(IV)] complex of (1a) which co-crystallises in small amount with the mononuclear component.

Results and Discussion

The preparation and properties of complexes (4a; M = VO) and (5a; M^1 = Cu, M^2 = VO) have been described elsewhere.[1,6] Complex (4b; M = VO) is prepared by the reaction of oxovanadium(IV) acetate and the macrocycle (2b) in ethanol. It is interesting to note that the macrocyclic complex is not formed, nor is it formed with the related macrocycles (2c) and (2d) where only the acyclic mononuclear products result.



(1)



(2)

	R
a	$[CH_2]_2$
b	$[CH_2]_3$
c	$[CH_2]_4$
d	$CH(Me)CH_2$

In contrast, with compound (2a) it is possible to isolate either the mononuclear macrocyclic or acyclic complex depending upon the water content of the solvent. From an absolute ethanol–chloroform mixture the macrocyclic species (6a; M = VO) is readily isolated but from 95% ethanol–chloroform the open-chain complex (4a; M = VO) is recovered. The mechanism for ring opening is not confirmed: it has been suggested that a metal-assisted hydrolysis occurs to open one diaminoethane bridge,[7,8] but it has also been observed that the free macrocycle is readily hydrolysed in the presence of dilute ethanoic acid to give the acyclic ligand.[6]

The structures of (4b; M = VO), (4a; M = VO) (monoclinic form), and (5a; M^1 = Cu, M^2 = VO) are illustrated in

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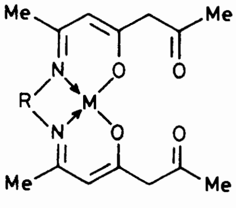
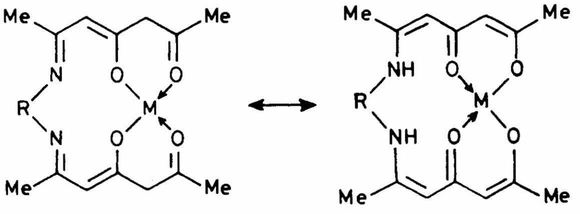
† *Supplementary data available* (No. SUP 23443, 83 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ The ligands present two adjacent, dissimilar compartments for complexation. The inner compartment is designated N_2O_2 and the outer compartment O_2O_2. For heterobinuclear complexes the metal in the inner compartment is mentioned before that in the outer compartment.



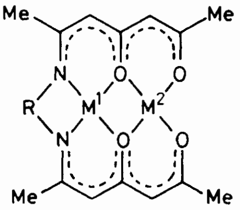
(3)

	R
a	$[CH_2]_2$
d	$CH(Me)CH_2$

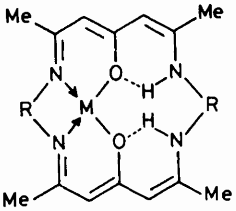


(4)

	R
a	$[CH_2]_2$
b	$[CH_2]_3$
c	$[CH_2]_4$
d	$CH(Me)CH_2$



(5)



(6)

	R
a	$[CH_2]_2$

Figures 1—3 respectively, in each case with the atom labelling used in the corresponding Tables [the molecular structure of the triclinic form of (4a; M = VO) is indistinguishable from that of the monoclinic form]. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments for all four structures are given in Tables 1—6.

In all four molecules a vanadyl unit is co-ordinated in the outer (O_2O_2) compartment with square-based pyramidal geometry, and the atoms of the basal plane are approximately coplanar. In the three monometallic complexes the vanadium atom lies quite close to the planes of each of the two bidentate diketone chelate rings, which are mutually inclined at *ca.* 44°: the vanadium is noticeably closer to these chelate planes in complex (4b; M = VO). In the bimetallic complex, the planes of the chelate rings are more nearly coplanar with the basal plane of the square-based pyramid, from which plane the vanadium is displaced by *ca.* 0.56 Å, as in the monometallic complexes. In this bimetallic complex, the inner (N_2O_2) site is occupied by a copper(II) ion in an approximately square, closely planar environment and again the planes of the bidentate keto-imine chelates are approximately coplanar with the co-ordination plane. In the two independent structures of complex (4a; M = VO) the di-iminoethane chelate fragment exhibits a normal, non-planar conformation (C–C torsion angles +52.3 and +52.1°), whereas in the bimetallic complex (5a; M^1 = Cu, M^2 = VO) with the same ligand the torsion angle is greatly reduced (+13.6°), presumably in order to provide the desired co-ordination geometry for the copper ion in the inner compartment. In each of the four molecules the planes of the four atoms defining each of the inner and outer compartments are fairly coincident, although in the two complexes (4a; M = VO) there is a markedly greater fold about the O(3) · · · O(4) line. Also, the adjacent diketone and keto-imine chelate planes are approximately coincident and the bond lengths indicate extensive electron delocalisation across each diketo-imine skeleton.

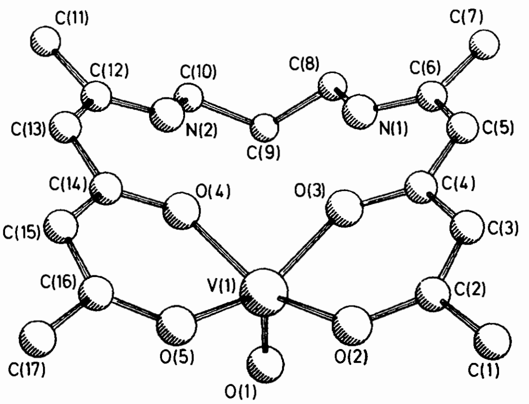


Figure 1. The molecular structure, with atom labelling, of complex (4b; M = VO)

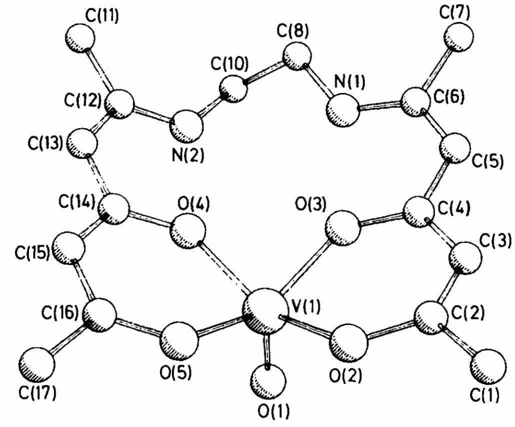


Figure 2. The molecular structure, with atom labelling, of complex (4a; M = VO), monoclinic form; the vanadyl unit, which occupies the inner site for a small proportion of the molecules, is omitted

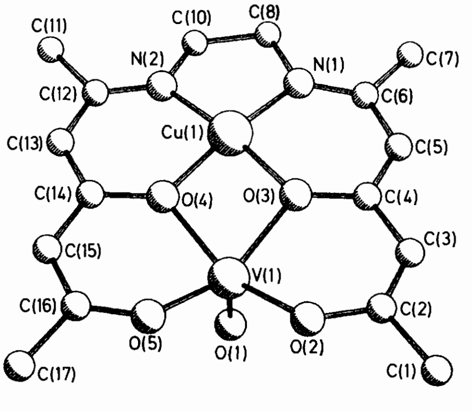


Figure 3. The molecular structure, with atom labelling, of complex (5a; M^1 = Cu, M^2 = VO)

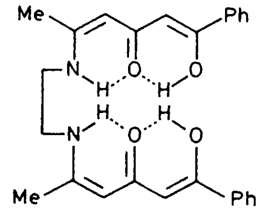
Table 1. Bond lengths (Å) and angles (°) with estimated standard deviations for the four molecules

	(4b; M = VO)·$CHCl_3$	(4a; M = VO)		(5a; M^1 = Cu, M^2 = VO)
		monoclinic	triclinic	
V(1)–O(1)	1.590(3)	1.602(9)	1.594(5)	1.600(5)
V(1)–O(2)	1.966(3)	1.941(8)	1.952(5)	1.934(5)
V(1)–O(3)	1.978(3)	1.987(8)	1.977(5)	1.994(5)
V(1)–O(4)	1.974(3)	1.980(8)	1.958(5)	1.981(5)
V(1)–O(5)	1.954(3)	1.954(9)	1.940(5)	1.937(5)
M–O(6)		1.60	1.60	
M–O(3)		1.92(6)	1.834(18)	1.902(5)
M–O(4)		1.96(6)	1.865(18)	1.904(5)
M–N(1)		1.81(6)	1.920(19)	1.871(6)
M–N(2)		1.89(6)	1.952(19)	1.892(6)
O(2)–C(2)	1.295(5)	1.326(15)	1.306(8)	1.324(9)
C(1)–C(2)	1.511(6)	1.484(20)	1.512(10)	1.511(11)
C(2)–C(3)	1.367(6)	1.346(18)	1.370(10)	1.346(10)
C(3)–C(4)	1.428(5)	1.434(18)	1.411(10)	1.438(10)
O(3)–C(4)	1.304(5)	1.316(15)	1.307(8)	1.323(8)
C(4)–C(5)	1.407(5)	1.439(17)	1.405(10)	1.391(10)
C(5)–C(6)	1.383(5)	1.353(18)	1.379(10)	1.401(11)
C(6)–C(7)	1.507(6)	1.531(20)	1.529(11)	1.527(12)
N(1)–C(6)	1.334(5)	1.315(17)	1.322(9)	1.314(10)
N(1)–C(8)	1.472(5)	1.488(20)	1.465(10)	1.442(11)
C(8)–C(9)	1.523(6)			
C(8)–C(10)		1.407(23)	1.477(12)	1.489(13)
O(1)–V(1)–O(2)	105.85(14)	105.6(4)	106.7(2)	106.3(3)
O(1)–V(1)–O(3)	106.39(14)	107.5(4)	107.3(2)	107.4(2)
O(1)–V(1)–O(4)	106.11(14)	107.2(4)	105.5(2)	105.8(2)
O(1)–V(1)–O(5)	107.12(14)	108.0(4)	107.3(2)	108.4(2)
O(2)–V(1)–O(3)	87.64(11)	87.7(3)	87.0(2)	86.7(2)
O(2)–V(1)–O(4)	148.03(11)	147.1(4)	147.7(2)	146.7(2)
O(2)–V(1)–O(5)	83.66(11)	84.2(4)	85.3(2)	91.2(2)
O(3)–V(1)–O(4)	82.54(11)	81.3(3)	81.6(2)	75.7(2)
O(3)–V(1)–O(5)	146.49(11)	144.6(4)	145.4(2)	143.2(2)
O(4)–V(1)–O(5)	87.93(11)	87.1(4)	87.1(2)	86.7(2)
O(6)–M–O(3)		84(3)	85.5(8)	
O(6)–M–O(4)		87(3)	88.2(8)	
O(6)–M–N(1)		95(3)	90.1(8)	
O(6)–M–N(2)		88(3)	85.4(8)	
O(3)–M–O(4)		84(2)	88.0(8)	79.7(2)
O(3)–M–N(1)		91(3)	90.2(8)	95.5(2)
O(3)–M–N(2)		168(4)	169.9(11)	172.4(2)
O(4)–M–N(1)		174(4)	177.6(11)	173.2(2)
O(4)–M–N(2)		87(3)	87.3(8)	94.2(2)
N(1)–M–N(2)		99(3)	94.2(8)	90.2(3)
V(1)–O(2)–C(2)	129.5(2)	129.5(8)	129.5(4)	123.5(5)
V(1)–O(3)–C(4)	131.4(2)	130.7(8)	132.2(4)	127.6(4)
V(1)–O(4)–C(14)	131.0(2)	131.3(8)	133.3(4)	129.9(4)
V(1)–O(5)–C(16)	129.2(3)	130.5(8)	129.3(4)	125.1(4)
M–O(3)–C(4)		129(2)	131.5(7)	127.4(4)
M–O(4)–C(14)		126(2)	126.8(7)	128.2(4)
M–N(1)–C(6)		128(2)	124.0(7)	124.9(5)
M–N(1)–C(8)		100(2)	102.6(7)	111.0(5)
M–N(2)–C(10)		97(2)	99.9(7)	110.2(5)
M–N(2)–C(12)		121(2)	118.9(7)	125.5(5)
V(1)–O(3)–M		98(2)	94.4(6)	100.1(2)
V(1)–O(4)–M		96(2)	94.1(6)	100.5(2)
C(9)–C(10)	1.515(6)			
N(2)–C(10)	1.461(6)	1.475(21)	1.480(11)	1.448(11)
N(2)–C(12)	1.333(5)	1.326(18)	1.335(9)	1.306(9)
C(11)–C(12)	1.511(6)	1.504(21)	1.515(12)	1.532(12)
C(12)–C(13)	1.373(6)	1.385(19)	1.385(10)	1.414(10)
C(13)–C(14)	1.425(6)	1.415(18)	1.418(10)	1.382(10)
O(4)–C(14)	1.295(5)	1.312(15)	1.300(8)	1.347(8)
C(14)–C(15)	1.415(6)	1.396(18)	1.412(10)	1.420(10)
C(15)–C(16)	1.371(6)	1.389(18)	1.365(10)	1.384(10)
C(16)–C(17)	1.505(6)	1.488(20)	1.518(11)	1.499(11)
O(5)–C(16)	1.291(5)	1.281(15)	1.298(8)	1.295(9)
Cl(1)–C(18)	1.745(5)			
Cl(2)–C(18)	1.764(5)			
Cl(3)–C(18)	1.743(5)			
O(3) ··· N(1)	2.676(4)	2.655(14)	2.660(8)	2.792(8)
O(4) ··· N(2)	2.675(4)	2.648(15)	2.636(8)	2.780(8)
N(1) ··· N(2)	3.297(5)	2.807(17)	2.836(9)	2.665(9)
O(3) ··· O(4)	2.607(4)	2.584(11)	2.570(6)	2.439(7)
O(2) ··· O(5)	2.614(4)	2.612(12)	2.637(7)	2.765(7)
V(1) ··· M		2.94(6)	2.798(18)	2.985 7(15)
O(1) ··· O(6)		3.10	2.89	
O(2)–C(2)–C(1)	113.9(3)	113.7(11)	113.6(6)	112.7(6)
O(2)–C(2)–C(3)	125.6(4)	125.5(11)	125.9(6)	127.1(7)
C(1)–C(2)–C(3)	120.5(4)	120.8(12)	120.6(6)	120.2(7)
C(2)–C(3)–C(4)	124.5(4)	124.4(12)	124.0(6)	125.1(7)
O(3)–C(4)–C(3)	121.3(3)	121.3(11)	121.1(6)	117.6(6)
O(3)–C(4)–C(5)	119.7(3)	117.6(11)	118.2(6)	120.0(6)
C(3)–C(4)–C(5)	119.0(3)	121.0(11)	120.7(6)	122.5(7)
C(4)–C(5)–C(6)	125.7(4)	125.0(12)	126.1(6)	128.3(7)
N(1)–C(6)–C(5)	122.8(4)	124.9(12)	123.4(6)	123.9(7)
N(1)–C(6)–C(7)	118.0(3)	116.1(12)	117.0(6)	119.1(7)
C(5)–C(6)–C(7)	119.2(4)	118.9(12)	119.6(6)	117.0(7)
C(6)–N(1)–C(8)	124.7(3)	128.3(12)	125.3(6)	124.0(7)
N(1)–C(8)–C(9)	112.2(3)			
N(1)–C(8)–C(10)		112.0(13)	110.2(7)	113.6(7)
C(8)–C(9)–C(10)	115.8(4)			
N(2)–C(10)–C(8)		112.8(14)	113.4(7)	113.7(7)
N(2)–C(10)–C(9)	112.4(4)			
C(10)–N(2)–C(12)	124.3(3)	129.8(13)	130.7(6)	124.3(7)
C(11)–C(12)–C(13)	118.9(4)	119.7(12)	119.0(7)	116.7(7)
N(2)–C(12)–C(11)	117.5(4)	118.5(12)	118.1(7)	119.5(7)
N(2)–C(12)–C(13)	123.6(4)	121.7(12)	122.9(7)	123.8(7)
C(12)–C(13)–C(14)	125.8(4)	127.1(12)	124.4(7)	128.3(7)
C(13)–C(14)–C(15)	119.5(4)	121.5(12)	120.8(6)	123.4(7)
O(4)–C(14)–C(13)	118.5(3)	117.1(11)	119.3(6)	119.3(6)
O(4)–C(14)–C(15)	122.0(4)	121.3(11)	119.8(6)	117.3(6)
C(14)–C(15)–C(16)	124.0(4)	124.9(12)	124.4(7)	125.1(7)
C(15)–C(16)–C(17)	120.2(4)	119.5(12)	121.2(7)	119.2(6)
O(5)–C(16)–C(15)	125.8(4)	124.2(12)	125.9(7)	126.4(7)
O(5)–C(16)–C(17)	113.9(4)	116.3(12)	112.9(6)	114.3(6)
Cl(1)–C(18)–Cl(2)	110.3(3)			
Cl(1)–C(18)–Cl(3)	110.7(3)			
Cl(2)–C(18)–Cl(3)	109.7(3)			

For both structures of (4a; M = VO), atom M represents the vanadium atom of partial occupancy in the inner site: for the structure (5a: M^1 = Cu, M^2 = VO), atom M represents the copper atom Cu(1) in the inner site.

Table 2. Planar fragments of complex (4b; M = VO). Equations of the planes are expressed as $pX + qY + rZ = d$; direction cosines are referred to orthogonal crystal axes a, b^*, c'. Deviations (Å) of selected atoms from the mean planes are given in square brackets

	p	q	r	d
Plane (A): V(1), O(2), O(3)				
	−0.9517	−0.0940	0.2924	−1.9901
[C(2) 0.022, C(3) −0.001, C(4) 0.003]				
Plane (B): V(1), O(4), O(5)				
	−0.8186	0.5639	−0.1095	0.3467
[C(14) −0.065, C(15) −0.084, C(16) −0.033]				
Plane (C): O(2)—O(5)				
	−0.9619	0.2544	0.1006	−1.4495
[O(2) 0.012, O(3) −0.012, O(4) 0.012, O(5) −0.012, V(1) 0.554, O(1) 2.144, C(2) −0.470, C(3) −0.758, C(4) −0.515, C(14) −0.555, C(15) −0.837, C(16) −0.543]				
Plane (D): O(2), O(3), C(2)—C(4)				
	−0.9530	−0.0932	0.2882	−1.9974
[O(2) −0.007, O(3) 0.002, C(2) 0.012, C(3) −0.009, C(4) 0.001, V(1) 0.002, C(1) 0.029, C(5) 0.033]				
Plane (E): O(4), O(5), C(14)—C(16)				
	−0.7973	0.5880	−0.1363	0.5101
[O(4) 0.007, O(5) −0.009, C(14) −0.005, C(15) −0.005, C(16) 0.012, V(1) −0.060, C(13) 0.004, C(17) 0.045]				
Plane (F): O(3), N(1), C(4)—C(6)				
	−0.9291	−0.0706	0.3629	−1.8195
[O(3) −0.011, N(1) −0.001, C(4) 0.022, C(5) −0.023, C(6) 0.012, C(7) 0.088]				
Plane (G): O(4), N(2), C(12)—C(14)				
	−0.7634	0.6378	−0.1016	0.8116
[O(4) −0.014, N(2) 0.006, C(12) 0.002, C(13) −0.016, C(14) 0.022, C(11) 0.037]				
Plane (H): O(3), O(4), N(1), N(2)				
	−0.9596	0.2550	0.1192	−1.4383
[O(3) −0.000, O(4) 0.000, N(1) 0.000, N(2) −0.000, V(1) 0.577, C(8) 0.399, C(9) 1.291, C(10) 0.571]				



(7)

A direct comparison may be made with the molecular structures of the related complexes of VO [9] and NiVO [10] with the acyclic ligand (7) derived from 1-phenylhexane-1,3,5-trione and 1,2-diaminoethane. The molecular dimensions vary very little; *e.g.* the VO distance is a little shorter in the compounds described in this work, and there are minor changes in the region of the CH_2CH_2 bridge. In both sets of compounds the V–O (outer compartment) is greater than the V–O (inner compartment) distance, and there is considerable delocalisation throughout the ligand framework. The Cu–V distance is 2.985 Å, marginally shorter than that found for Ni–V (2.991 Å) and the Cu–O–VO bridge angles are 100.1 and 100.5°. The C–C distance in the CH_2CH_2 bridge is reduced from the normal single-bond distance in complexes (4a; M = VO) and (5a; M^1 = Cu, M^2 = VO) but such lengths remain normal in (4b; M = VO). This reduction has been ascribed to a strain inherent in the bridge on encapsulation of the second metal.[10] It has, however, also been noted that there is a shortening of the C–C bond in some diaminoethane and polyether species.[11] The origin of the shortening remains conjectural; it is not certain whether it is an artefact or a consequence of the relative freedom of the bridge to vibrate giving a lowered apparent bond length.

Table 3. Planar fragments of complex (4a; M = VO) (monoclinic form). Details as in Table 2 except that direction cosines are referred to orthogonal crystal axes a, b, c^*

	p	q	r	d
Plane (A): V(1), O(2), O(3)				
	−0.4998	−0.8550	−0.1387	−3.8209
[C(2) 0.167, C(3) 0.260, C(4) 0.108]				
Plane (B): V(1), O(4), O(5)				
	−0.3869	−0.4251	−0.8183	−2.0359
[C(14) −0.031, C(15) 0.033, C(16) 0.110]				
Plane (C): O(2)—O(5)				
	−0.4869	−0.6987	−0.5243	−3.7793
[O(2) 0.022, O(3) −0.023, O(4) 0.023, O(5) −0.022, V(1) 0.577, O(1) 2.178, C(2) −0.359, C(3) −0.553, C(4) −0.454, C(14) −0.536, C(15) −0.752, C(16) −0.433]				
Plane (D): O(2), O(3), C(2)—C(4)				
	−0.4913	−0.8313	−0.2600	−3.8770
[O(2) −0.009, O(3) 0.021, C(2) −0.002, C(3) 0.024, C(4) −0.034, V(1) 0.180, C(1) −0.027, C(5) −0.194, V(2) −0.563]				
Plane (E): O(4), O(5), C(14)—C(16)				
	−0.3723	−0.4539	−0.8096	−2.1215
[O(4) 0.032, O(5) −0.039, C(14) −0.030, C(15) −0.011, C(16) 0.048, V(1) 0.026, C(13) −0.214, C(17) 0.170, V(2) −0.748]				
Plane (F): O(3), N(1), C(4)—C(6)				
	−0.3367	−0.9036	−0.2650	−3.4937
[O(3) 0.022, N(1) −0.010, C(4) −0.034, C(5) 0.024, C(6) −0.002, C(7) −0.059, V(2) −0.324, O(6) 1.218]				
Plane (G): O(4), N(2), C(12)—C(14)				
	−0.2674	−0.4210	−0.8668	−1.4588
[O(4) −0.028, N(2) 0.031, C(12) −0.037, C(13) 0.008, C(14) 0.026, C(11) −0.130, V(2) −0.789, O(6) 0.580]				
Plane (H): O(3), O(4), N(1), N(2)				
	−0.3494	−0.8112	−0.4689	−3.5919
[O(3) 0.082, O(4) −0.082, N(1) −0.075, N(2) 0.076, V(1) 0.335 C(8) −0.256, C(10) 0.414, V(2) −0.047, O(6) 1.549]				

In complex (4b; M = VO) the imino hydrogen atoms were unambiguously detected in positions in which they were clearly engaged in hydrogen bonding to the central oxygen atom of the diketo-imine fragment. However, in the two independent structures of (4a; M = VO) there was little evidence for hydrogen atoms in such positions; rather, in each case, there appeared a small but compact peak in the centre of the inner compartment. Attempts to utilise this peak for two disordered hydrogen atoms engaging in extensive intracompart-

Table 4. Planar fragments of complex (4a; M = VO) (triclinic form). Details as in Table 2

	p	*q*	*r*	*d*
Plane (A): V(1), O(2), O(3)				
	−0.0547	0.8699	−0.4902	−1.8420
[C(2) 0.097, C(3) 0.161, C(4) 0.091]				
Plane (B): V(1), O(4), O(5)				
	−0.6952	0.4125	−0.5887	−3.2796
[C(14) −0.073, C(15) −0.096, C(16) −0.030]				
Plane (C): O(2)—O(5)				
	−0.4046	0.6973	−0.5916	−3.3194
[O(2) 0.019, O(3) −0.019, O(4) 0.020, O(5) −0.019, V(1) 0.562, O(1) 2.156, C(2) −0.405, C(3) −0.620, C(4) −0.447, C(14) −0.564, C(15) −0.859, C(16) −0.557]				
Plane (D): O(2), O(3), C(2)—C(4)				
	−0.1272	0.8484	−0.5138	−2.1864
[O(2), 0.001, O(3) 0.004, C(2) −0.005, C(3) 0.009, C(4) −0.008, V(1) 0.115, C(1) −0.057, C(5) −0.091, V(2) −0.533]				
Plane (E): O(4), O(5), C(14)—C(16)				
	−0.7251	0.3796	−0.5746	−3.2886
[O(4) 0.008, O(5) −0.013, C(14) −0.005, C(15) −0.008, C(16) 0.018, V(1) −0.067, C(13) −0.054, C(17) 0.061, V(2) −0.749]				
Plane (F): O(3), N(1), C(4)—C(6)				
	−0.1508	0.8852	−0.4401	−2.4643
[O(3) −0.003, N(1) 0.012, C(4) −0.007, C(5) 0.020, C(6) −0.023, C(7) −0.100, V(2) −0.437, O(6) 1.096]				
Plane (G): O(4), N(2), C(12)—C(14)				
	−0.7521	0.3539	−0.5559	−3.2828
[O(4) −0.021, N(2) 0.027, C(12) −0.035, C(13) 0.013, C(14) 0.016, C(11) −0.124, V(2) −0.801, O(6) 0.568]				
Plane (H): O(3), O(4), N(1), N(2)				
	−0.3786	0.7620	−0.5254	−3.4617
[O(3) 0.063, O(4) −0.063, N(1) −0.057, N(2) 0.058, V(1) 0.460, C(8) −0.283, C(10) 0.393, V(2) −0.089, O(6) 1.512]				

Table 5. Planar fragments of complex (5a; M^1 = Cu, M^2 = VO). Details as in Table 3

	p	*q*	*r*	*d*
Plane (A): V(1), O(2), O(3)				
	−0.7712	0.2941	0.5646	−1.7019
[C(2) −0.597, C(3) −0.920, C(4) −0.637]				
Plane (B): V(1), O(4), O(5)				
	−0.8536	−0.4475	0.2667	−2.2681
[C(14) −0.525, C(15) −0.809, C(16) −0.547]				
Plane (C): O(2)—O(5)				
	−0.8749	−0.0940	0 4751	−1.6531
[O(2) −0.029, O(3) 0.033, O(4) −0.033, O(5) 0.029, V(1) −0.573, O(1) −2.173, C(2) −0.101, C(3) −0.145, C(4) −0.085, C(14) −0.014, C(15) −0.026, C(16) −0.009]				
Plane (D): O(2), O(3), C(2)—C(4)				
	−0.8870	−0.1572	0.4343	−1.5697
[O(2) −0.010, O(3) 0.009, C(2) 0.012, C(3) −0.002, C(4) −0.010, V(1) −0.671, C(1) 0.076, C(5) −0.023, Cu(1) −0.078]				
Plane (E): O(4), O(5), C(14)—C(16)				
	−0.8672	−0.0913	0.4896	−1.6646
[O(4) −0.014, O(5) 0.012, C(14) 0.017, C(15) −0.005, C(16) −0.010, V(1) −0.586, C(13) 0.065, C(17) −0.004, Cu(1) 0.080]				
Plane (F): O(3), N(1), C(4)—C(6)				
	−0.8743	−0.1707	0.4545	−1.5830
[O(3) 0.004, N(1) 0.001, C(4) −0.010, C(5) 0.012, C(6) −0.007, C(7) −0.038, C(8) −0.032, Cu(1) −0.046]				
Plane (G): O(4), N(2), C(12)—C(14)				
	−0.8689	−0.1292	0.4779	−1.7596
[O(4) 0.007, N(2) 0.000, C(12) −0.008, C(13) 0.015, C(14) −0.015, C(10) −0.111, C(11) −0.032, Cu(1) 0.157]				
Plane (H): O(3), O(4), N(1), N(2)				
	−0.8615	−0.0797	0.5014	−1.6524
[O(3) 0.001, O(4) −0.001, N(1) −0.001, N(2) 0.001, V(1) −0.603, C(8) 0.032, C(10) −0.142, Cu(1) 0.082]				

ment hydrogen bonding were unsuccessful and indicated that the peak corresponded to a rather greater, more compact electron density. In view of our detection (from mass spectral results) of small quantities of the otherwise un-isolated complex (5a; $M^1 = M^2$ = VO) during the preparation of (4a; M = VO), the possibility was investigated that such molecules might have co-crystallised along with the monometallic complex, in both monoclinic and triclinic crystalline forms. Occupancy factors of 0.036(4) and 0.065(2) respectively were determined for vanadiums in the inner sites (B = 3.2 and 3.1 Å^2 respectively); the associated vanadyl oxygen atoms were included in calculated positions (V–O 1.60 Å, B = 5.0 and 4.0 Å^2) although, not surprisingly, little evidence for their presence was found; hydrogen atoms on the imino-nitrogen atoms were included in calculated positions with appropriately reduced occupancies. It is noteworthy that the conformation adopted by the chelate groups defining the inner compartment is ideal for the co-ordination of a second vanadyl unit, although the compartment is slightly large. The possibility that, at least in the case of the triclinic crystalline form, the occupant of this site could be a copper(II) ion may be discounted in view of the markedly different conformation adopted by the ligand in the mixed bimetallic (5a; M^1 = Cu, M^2 = VO) and the absence of any suggestion of the necessarily consequential ligand disorder in either of these predominantly monometallic (4a; M = VO) structures. In neither (4a; M = VO) crystal structure is there any intra- or inter-molecular packing constraint which would prohibit the co-ordination of a vanadyl unit in the inner site, thus facilitating the co-crystallisation of the two molecules. The slight non-coplanarity of the inner and outer compartments serves to increase the intramolecular separation of the vanadyl oxygen atoms. The crystal and molecular packing of (4b; M = VO) precludes such co-crystallisation; in particular, one of the hydrogen atoms on the central carbon atom of the di-iminopropane fragment [C(9)] would lie very close to the site for the vanadyl oxygen atom. Figure 4 illustrates the proposed structure of complex (5a; $M^1 = M^2$ = VO) in its triclinic modification; that of the monoclinic modification is indistinguishable.

It seems that the greater deviations from regularity of the (4a; M = VO) complexes as compared to the much more regular structure (approximate C_s symmetry) of (4b; M = VO) activate the former to the relatively facile co-ordination of a further vanadyl unit. However, it is not clear why two

Table 6. Selected interplanar angles (°) for the four structures (planes are as defined in the preceding four Tables)

	(4b; M = VO)	(4a; M = VO)		(5a; M^1 = Cu, M^2 = VO)		(4b; M = VO)	(4a; M = VO)		(5a; M^1 = Cu, M^2 = VO)
		monoclinic	triclinic				monoclinic	triclinic	
(A)–(B)	46.1	47.9	46.7	47.4	(C)–(F)	24.2	20.9	20.2	4.6
(A)–(C)	22.9	24.0	23.3	23.7	(C)–(G)	27.6	28.5	28.4	2.0
(A)–(D)	0.3	7.1	4.5	28.0	(C)–(H)	1.1	10.7	5.5	1.9
(A)–(F)	4.4	12.2	6.3	28.3	(D)–(E)	48.3	39.6	44.8	5.1
(B)–(C)	23.1	23.9	23.5	23.7	(D)–(F)	4.7	9.8	4.9	1.6
(B)–(E)	2.4	1.9	2.7	24.3	(E)–(G)	4.0	7.1	2.4	2.3
(B)–(G)	5.3	7.4	5.0	22.0	(F)–(G)	51.1	45.6	47.8	2.7
(C)–(D)	22.8	17.0	18.7	4.4	(F)–(H)	23.5	12.9	15.7	5.9
(C)–(E)	25.5	22.7	26.1	1.0	(G)–(H)	28.0	32.7	32.2	3.2

Torsion angles (°) for the di-iminoalkane fragments

	(4b; M = VO)		(4a; M = VO)		(5a; M^1 = Cu, M^2 = VO)
			monoclinic	triclinic	
C(6)–N(1)–C(8)–C(9)	+164.4	C(6)–N(1)–C(8)–C(10)	+166.5	+174.1	+165.5
N(1)–C(8)–C(9)–C(10)	+86.5	N(1)–C(8)–C(10)–N(2)	+52.3	+52.1	+13.6
C(8)–C(9)–C(10)–N(2)	−75.3	C(8)–C(10)–N(2)–C(12)	+105.3	+107.3	+170.6
C(9)–C(10)–N(2)–C(12)	−176.5				

Table 7. Important intermolecular contacts (distances in Å, angles in °) in the four molecules

(4b; M = VO)·$CHCl_3$	
O(2) $\cdots$ C(18^{I})	3.139(5)
O(2) $\cdots$ H(18^{I})	2.18
V(1) $\cdots$ H(18^{I})	3.30
O(2) $\cdots$ H(18′)–C(18′)	175
(4a; M = VO) (monoclinic form)	
O(6) $\cdots$ N(1^{II})	2.76
O(6) $\cdots$ C(6^{II})	2.76
(4a; M = VO) (triclinic form)	
O(6) $\cdots$ N(1^{II})	2.65
O(6) $\cdots$ C(6^{II})	2.72
(5a; M^1 = Cu, M^2 = VO)	
Cu(1) $\cdots$ O(3^{III})	3.222(5)
O(3)–Cu(1) $\cdots$ O(3^{III})	91.3(2)
O(4)–Cu(1) $\cdots$ O(3^{III})	92.2(2)
N(1)–Cu(1) $\cdots$ O(3^{III})	92.8(2)
N(2)–Cu(1) $\cdots$ O(3^{III})	93.6(2)

Roman numeral superscripts indicate the following symmetry equivalent positions: I $1 - x, 1 - y, 1 - z$; II $1 - x, -y, -z$; III $-x, -y, -z$.

distinct crystalline forms of the chemically indistinguishable molecules are produced from similar sources.

Other geometrical features of the four molecules are normal and require no further comment. In the crystal structure of complex (4b; M = VO), a chloroform molecule of solvation seems to engage in weak hydrogen bonding to atom O(2) *via* an almost linear C–H $\cdots$ O interaction. In both structures of the co-crystallised (4a; M = VO) and (5a; $M^1 = M^2$ = VO) there is a short intermolecular contact between the oxygen atom of the partial occupancy vanadyl unit [O(6)] and an imino-nitrogen atom of a molecule related by an inversion centre [N(1)] (2.76 and 2.65 Å respectively). These distances suggest the formation of a strong hydrogen bond between the bimetallic complex (where present) and an adjacent monometallic complex, thereby imposing a limit of 50% on the degree of co-crystallisation of the bimetallic complex, a proportion not approached in the structures analysed here. In both structures, the final difference-Fourier syntheses show residual electron density in positions appropriate for such an intermolecular hydrogen bond. In the crystal structure of complex (5a; M^1 = Cu, M^2 = VO) a bridging oxygen atom [O(3)] of a molecule related by the inversion centre is situated directly below the copper atom at a distance of 3.222(5) Å on the opposite side of the mean molecular plane to the vanadyl oxygen atom. The marked deviation of the copper atom from the plane of the atoms of the inner co-ordination site is in a direction towards this intermolecular contact. Table 7 summarises the significant intermolecular contacts in the four structures.

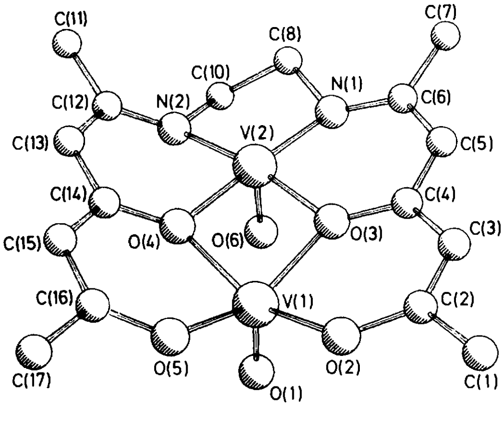
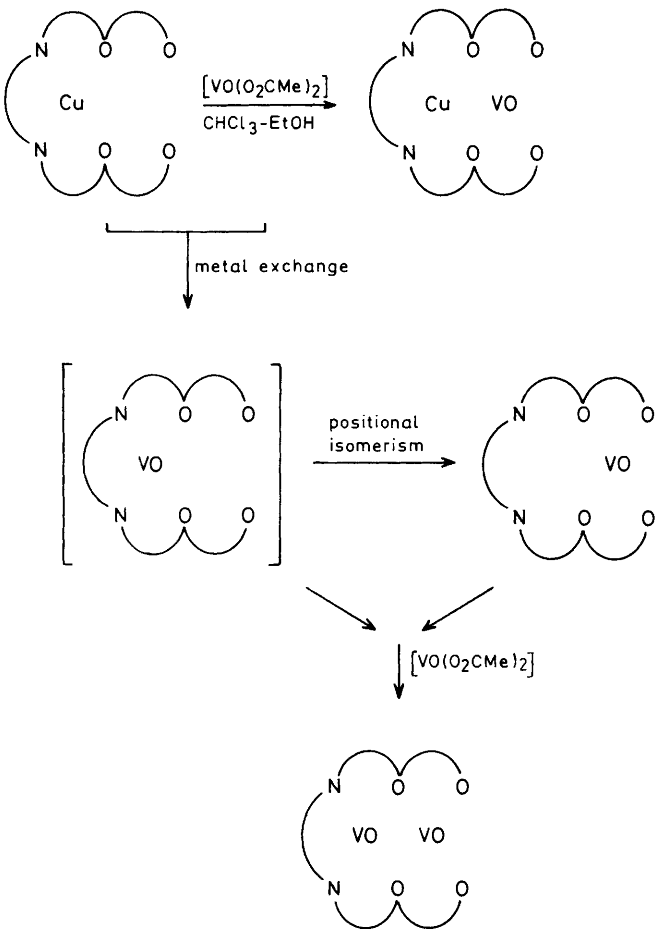


Figure 4. The molecular structure, with atom labelling, of complex (5a; $M^1 = M^2$ = VO), triclinic form; the vanadyl unit, which occupies the inner site in only a small proportion of the molecules, is shown

The presence of both mono- and homobi-nuclear oxovanadium(IV) complexes in the product from the heterobinuclear preparation was unexpected and the mechanism of formation is not obvious. One possibility is that any presence of HCl in the $CHCl_3$ solvent used for recrystallising the bulk sample could strip the metals from the ligand and allow the subsequent reincorporation of oxovanadium(IV) into the

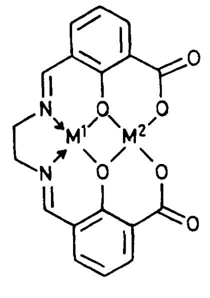


Scheme.

outer compartment. An alternative scheme, suggesting a route for incorporation during the synthesis, is depicted above.

The first step is replacement of some copper(II) by oxovanadium(IV); this type of metal exchange has been detected in the reaction of nickel(II) with complex (3a; M = Cu) to yield (3a; M = Ni).[1] As oxovanadium(IV) prefers an all-oxygen environment, positional isomerism can occur, probably *via* an intramolecular rearrangement, to give (4a; M = VO).* Both isomers would be capable of adding a second oxovanadium(IV) to give the homobinuclear complex which then co-crystallises with the bulk product.

This behaviour suggests that there is a complex solution chemistry for the heterobinuclear complexes. It is probable that there are several species present in solution and that the product isolated is a function of the insolubility of individual species. The observations advocate caution in the interpretation of reactivity studies made with such species in solution. Similar trends have been noted during the synthesis of complex (5a; M^1 = Cu, M^2 = Zn) from (3a; M = Cu) where a (5a; M^1 = M^2 = Cu) fraction was isolated,[1] and in the preparation of (8; M^1 = Cu, M^2 = VO) where also a (8; M^1 = M^2 = Cu) complex was obtained.[13,†]



(8)

Experimental

Heptane-2,4,6-trione and its macrocyclic Schiff bases were synthesised according to reported methods.[5] The complex (5a; M^1 = Cu, M^2 = VO) was prepared as previously described.[1] The acyclic metal complexes were prepared by the following methods.

Method (1). The macrocyclic Schiff base (0.01 mol) dissolved in the minimum volume of hot chloroform was added to a suspension of oxovanadium(IV) acetate (0.01 mol) in the minimum volume of 95% ethanol or absolute ethanol. The resulting mixture was refluxed overnight and the solution filtered whilst hot to remove any unreacted oxovanadium(IV) acetate. On cooling either powders or crystalline solids were recovered. The complexes were redissolved in chloroform and light petroleum (b.p. 60–80 °C) added to effect crystallisation as dark green crystalline solids. In the case of the reaction of VO^{2+} with compound (2a) two products were recovered depending on the solvent used; an acyclic product was obtained from 95% EtOH–$CHCl_3$ and a macrocyclic product from absolute EtOH–$CHCl_3$.

Method (2). The acyclic complexes were also prepared by refluxing for 1.5 h a mixture of the Schiff-base macrocycle dissolved in chloroform and oxovanadium(IV) acetate suspended in water. After filtering whilst hot, separating the $CHCl_3$ layer, and drying over $MgSO_4$, the mononuclear complex was recovered on evaporation of the solvent.

Complex (6a; M = VO): P^+ = 397, M = 397 (Found: C, 54.1; H, 6.6; N, 13.4. Calc. for $C_{18}H_{26}N_4O_3V$: C, 54.4; H, 6.5; N, 14.1). (4a; M = VO): P^+ = 373, 428; M = 373 (4a), 438 (5a; M^1 = M^2 = VO) (Found: C, 52.0; H, 6.0; N, 8.0. Calc. for $C_{16}H_{22}N_2O_5V$: C, 51.4; H, 5.9; N, 7.5). (4b; M = VO)·$CHCl_3$: P^+ = 387, M = 387 (4b) (Found: C, 42.8; H, 4.5; Cl, 21.1; N, 5.5. Calc. for $C_{18}H_{25}Cl_3N_2O_5V$: C, 42.6; H, 4.9; Cl, 21.0; N, 5.5). (4c; M = VO): P^+ = 401, M = 401 (Found: C, 53.7; H, 6.5; N, 7.0. Calc. for $C_{18}H_{26}N_2O_5V$: C, 53.8; H, 6.5; N, 7.0). (4d; M = VO) (Found: C, 52.3; H, 6.2; N, 7.0. Calc. for $C_{17}H_{24}N_2O_5V$: C, 52.7; H, 6.2; N, 7.2%).

Crystal Data.—(4b; M = VO)·$CHCl_3$. $C_{18}H_{25}Cl_3N_2O_5V$, M = 506.70, crystallises from chloroform–light petroleum as thick green plates, crystal dimensions 0.354 × 0.12 × 0.338 mm, triclinic, a = 10.966(5), b = 8.358(4), c = 15.226(8) Å, α = 92.36(8), β = 123.77(11), γ = 102.16(10)°, U = 1 112.3(11) Å^3, D_m = 1.49, Z = 2, D_c = 1.513 g cm^{-3}, space group

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* A site exchange has been observed in the preparation of (3d; M = Cu). A purple oil is first recovered and identified as the N_2O_2 isomer from its optical and i.r. spectra. On standing dark green crystals of the O_2O_2 isomer are produced, and the spectral data are consistent with this designation.[12]

† *Note added in proof.* The synthesis and crystal structure of (8; M^1 = Cu, M^2 = VO) was published while this paper was being considered for publication.[14] The Cu–VO distance is 2.989 Å and details are also given for the compound in which the structure appears to have a random distribution of CuVO and CuCu site occupancies with proportions of 85% and 15% respectively.

Table 8. Atomic positional parameters with estimated standard deviations

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
(4b; M = VO)·$CHCl_3$ [a]							
V(1)	0.408 09(6)	0.496 77(7)	0.173 72(4)	C(5)	0.266 4(4)	−0.032 6(4)	0.071 3(3)
Cl(1)	0.140 90(15)	0.174 13(20)	0.468 00(11)	C(6)	0.135 0(4)	−0.063 6(4)	−0.032 2(3)
Cl(2)	0.302 45(14)	0.370 26(14)	0.393 16(8)	C(7)	0.046 9(4)	−0.241 4(5)	−0.091 2(3)
Cl(3)	0.437 95(17)	0.151 07(17)	0.536 95(13)	C(8)	−0.064 0(4)	0.031 0(4)	−0.189 2(3)
O(1)	0.291 2(3)	0.546 2(3)	0.192 8(2)	C(9)	−0.116 1(4)	0.188 7(5)	−0.211 6(3)
O(2)	0.554 2(3)	0.427 4(3)	0.306 1(2)	C(10)	−0.051 7(4)	0.305 1(5)	−0.258 8(3)
O(3)	0.318 1(3)	0.258 6(3)	0.103 1(2)	C(11)	0.121 6(5)	0.528 0(6)	−0.314 6(3)
O(4)	0.339 3(3)	0.528 8(3)	0.026 9(2)	C(12)	0.188 3(4)	0.516 2(5)	−0.198 4(3)
O(5)	0.578 7(3)	0.696 6(3)	0.228 9(2)	C(13)	0.326 3(4)	0.626 2(5)	−0.119 0(3)
N(1)	0.080 8(3)	0.057 8(3)	−0.082 3(2)	C(14)	0.400 4(4)	0.637 3(4)	−0.006 0(3)
N(2)	0.107 6(3)	0.399 5(4)	−0.178 8(2)	C(15)	0.535 9(4)	0.767 0(4)	0.066 6(3)
C(1)	0.691 6(4)	0.275 9(5)	0.437 8(3)	C(16)	0.614 0(4)	0.790 2(4)	0.176 5(3)
C(2)	0.565 3(4)	0.279 1(4)	0.323 6(3)	C(17)	0.755 2(4)	0.934 3(5)	0.247 3(3)
C(3)	0.476 7(4)	0.134 4(4)	0.248 6(3)	C(18)	0.320 5(5)	0.282 8(5)	0.501 9(3)
C(4)	0.353 1(4)	0.124 9(4)	0.139 6(3)				
(4a; M = VO) (monoclinic form) [b]							
V(1)	0.243 0(2)	0.133 85(9)	−0.030 3(2)	C(6)	0.678 5(13)	0.044 4(5)	0.285 2(15)
O(1)	0.137 5(9)	0.086 5(4)	−0.132 8(11)	C(7)	0.821 0(16)	0.018 9(7)	0.388 9(18)
O(2)	0.161 0(9)	0.150 2(4)	0.164 5(10)	C(8)	0.808 4(16)	0.057 3(8)	0.045 2(19)
O(3)	0.408 2(9)	0.094 3(3)	0.121 9(10)	C(10)	0.763 8(20)	0.058 6(7)	−0.130 2(19)
O(4)	0.402 4(9)	0.148 9(4)	−0.153 0(10)	C(11)	0.818 9(16)	0.162 9(8)	−0.317 6(20)
O(5)	0.162 1(9)	0.207 8(4)	−0.107 7(10)	C(12)	0.675 6(13)	0.153 0(6)	−0.262 1(15)
N(1)	0.679 6(13)	0.055 9(5)	0.128 1(13)	C(13)	0.566 3(15)	0.194 1(6)	−0.290 6(16)
N(2)	0.656 4(12)	0.104 1(6)	−0.190 1(15)	C(14)	0.429 1(14)	0.193 0(5)	−0.239 4(14)
C(1)	0.101 1(16)	0.148 2(7)	0.430 4(18)	C(15)	0.331 2(15)	0.238 6(5)	−0.268 8(16)
C(2)	0.201 4(13)	0.130 8(6)	0.319 6(13)	C(16)	0.201 0(14)	0.242 8(5)	−0.210 0(15)
C(3)	0.320 8(14)	0.098 3(6)	0.377 8(15)	C(17)	0.100 3(18)	0.291 7(6)	−0.261 6(20)
C(4)	0.428 1(13)	0.082 5(5)	0.282 4(14)	V(2)	0.551(7)	0.100(3)	−0.016(7)
C(5)	0.563 6(14)	0.054 5(5)	0.360 0(15)	O(6)	0.461	0.048	−0.113
(4a; M = VO) (triclinic form) [b]							
V(1)	0.507 95(15)	−0.271 58(11)	−0.227 75(14)	C(6)	0.756 5(8)	−0.083 5(6)	0.201 3(7)
O(1)	0.412 3(6)	−0.177 9(4)	−0.357 6(5)	C(7)	0.838 7(10)	−0.029 2(7)	0.343 2(9)
O(2)	0.710 0(5)	−0.290 8(4)	−0.294 1(5)	C(8)	0.506 1(10)	−0.111 1(7)	0.310 9(9)
O(3)	0.637 7(5)	−0.192 5(4)	−0.062 6(5)	C(10)	0.332 2(10)	−0.126 3(7)	0.247 3(10)
O(4)	0.373 3(5)	−0.312 2(4)	−0.067 9(5)	C(11)	0.147 3(11)	−0.344 0(9)	0.341 1(10)
O(5)	0.442 8(6)	−0.417 4(4)	−0.291 5(5)	C(12)	0.224 3(8)	−0.323 7(6)	0.196 6(8)
N(1)	0.599 5(7)	−0.105 9(5)	0.186 1(6)	C(13)	0.215 3(8)	−0.409 2(6)	0.107 3(9)
N(2)	0.294 4(7)	−0.222 4(5)	0.159 0(7)	C(14)	0.290 4(8)	−0.403 3(6)	−0.024 6(8)
C(1)	0.980 2(9)	−0.281 6(7)	−0.329 5(9)	C(15)	0.279 9(8)	−0.495 9(6)	−0.106 2(9)
C(2)	0.855 2(8)	−0.251 2(6)	−0.243 7(8)	C(16)	0.350 6(8)	−0.497 4(6)	−0.232 5(8)
C(3)	0.898 5(8)	−0.189 3(6)	−0.123 6(8)	C(17)	0.328 8(10)	−0.598 9(7)	−0.317 5(10)
C(4)	0.790 6(8)	−0.162 2(5)	−0.033 0(7)	V(2)	0.483 9(21)	−0.212 5(15)	0.061 0(19)
C(5)	0.846 4(8)	−0.105 5(6)	0.095 7(8)	O(6)	0.3950	−0.1109	−0.0611
(5a; M^1 = Cu, M^2 = VO)							
Cu(1)	0.219 58(12)	0.030 71(9)	0.002 52(6)	C(5)	0.117 1(10)	−0.198 1(6)	−0.087 4(4)
V(1)	0.015 82(14)	0.137 45(9)	−0.147 20(6)	C(6)	0.247 9(9)	−0.200 2(6)	−0.015 5(4)
O(1)	0.152 8(6)	0.149 2(4)	−0.191 5(3)	C(7)	0.332 2(11)	−0.311 6(7)	0.011 8(5)
O(2)	−0.184 2(6)	0.073 0(4)	−0.221 5(3)	C(8)	0.436 4(11)	−0.114 6(7)	0.102 5(5)
O(3)	0.053 1(6)	−0.008 6(4)	−0.093 7(3)	C(10)	0.501 0(11)	−0.002 8(7)	0.131 6(5)
O(4)	0.138 0(6)	0.173 1(4)	−0.036 4(3)	C(11)	0.548 3(11)	0.220 2(8)	0.189 6(5)
O(5)	−0.098 6(6)	0.277 9(4)	−0.152 6(3)	C(12)	0.410 8(9)	0.189 3(7)	0.112 9(4)
N(1)	0.300 6(7)	−0.112 9(5)	0.028 8(3)	C(13)	0.310 2(9)	0.276 5(6)	0.070 1(4)
N(2)	0.391 7(7)	0.086 1(5)	0.091 0(3)	C(14)	0.183 6(8)	0.271 7(6)	−0.001 6(4)
C(1)	−0.331 4(10)	−0.053 1(7)	−0.319 6(4)	C(15)	0.097 5(9)	0.366 3(6)	−0.041 6(4)
C(2)	−0.195 5(8)	−0.032 3(6)	−0.242 2(4)	C(16)	−0.033 3(8)	0.364 6(6)	−0.112 2(4)
C(3)	−0.102 7(9)	−0.116 7(6)	−0.201 8(4)	C(17)	−0.115 3(10)	0.471 2(6)	−0.146 8(4)
C(4)	0.025 2(8)	−0.107 6(5)	−0.126 3(4)				

[a] Atoms Cl(1)—Cl(3) and C(18) comprise the chloroform molecule of solvation. [b] Atoms V(2) and O(6) are those of the vanadyl unit of low occupancy in the inner site.

$P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 8.25 cm^{-1}, $F(000)$ = 522.

Three-dimensional X-ray diffraction data were collected (in an $F\bar{1}$ setting) in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the ω-scan method. 2 985 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption: a correction was made for 38% intensity loss during data collection, based on the monitoring of two reflections. The structure was solved by superposition, Patterson, and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions (C–H 0.95, N–H 0.91 Å, methyl C–C–H 110°); their contributions were included in structure-factor calculations (B = 7.0 Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0385 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of vanadium and chlorine. Table 8 lists the atomic positional parameters, with estimated standard deviations, for all four molecules.

(4a; M = VO). $C_{16}H_{21.928}N_2O_{5.036}V_{1.036}$, M = 375.64, green needles from chloroform, crystal dimensions 0.04 × 0.06 × 0.15 mm, monoclinic, a = 9.230(3), b = 23.657(15), c = 8.177(6) Å, β = 102.160(14)°, U = 1 745(2) Å^3, D_m = 1.42, Z = 4, D_c = 1.43 g cm^{-3}, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 5.93 cm^{-1}, $F(000)$ = 784.176.

The data were collected and processed (987 independent reflections, absorption corrections not applied) as for (4b; M = VO)·$CHCl_3$ above; no intensity loss was detected during data collection. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares (R 0.0638).

$C_{16}H_{21.87}N_2O_{5.065}V_{1.065}$, M = 377.52, light green plates from chloroform, crystal dimensions 0.06 × 0.18 × 0.23 mm, triclinic, a = 8.459(6), b = 12.002(9), c = 8.789(7) Å, α = 80.140(7), β = 101.447(12), γ = 93.946(7)°, U = 861(1) Å^3, D_m = 1.43, Z = 2, D_c = 1.46 g cm^{-3}, space group $P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 6.15 cm^{-1}, $F(000)$ = 393.77.

The data were collected and processed (1 598 independent reflections) and the structure solved and refined (R 0.0545) as for the monoclinic modification above. The hydrogen atoms of the methyl groups were approximated by six half-population hydrogen atoms distributed around the annulus.

(5a; M^1 = Cu, M^2 = VO). $C_{16}H_{20}CuN_2O_5V$, M = 434.82, crystallises from the same chloroform solution as yielded the triclinic modification of (4a; M = VO) as dark green bricks, crystal dimensions 0.15 × 0.17 × 0.53 mm, monoclinic, a = 8.325(20), b = 12.117(11), c = 18.105(18) Å, β = 108.93(6)°, U = 1 727(4) Å^3, D_m = 1.65, Z = 4, D_c = 1.67 g cm^{-3}, space group $P2_1/c$, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 17.21 cm^{-1}, $F(000)$ = 888.

The data were collected and processed (2 480 independent reflections) and the structure solved and refined (R 0.0613) as for the monoclinic modification of (4a; M = VO).

Scattering factors were taken from ref. 15. Unit weights were used throughout the refinements. The computer programs used were SHELX and those of the Sheffield X-ray system.

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