SUPPLEMENTARY INFORMATION

Table S1 Selected bond lengths (Å) and angles (º) for **1** and **2**.

Bond lengths (Å)			Angles (º)		
	1	**2**		**1**	**2**
V(1)–O(1)	1.926(3)	1.915(3)	O(2)–V(1)–O(3)	105.86(14)	107.06(13)
V(1)–O(2)	1.614(3)	1.622(3)	O(2)–V(1)–O(1)	102.74(13)	102.08(12)
V(1)–O(3)	1.679(2)	1.667(4)	O(3)–V(1)–O(1)	98.18(12)	97.43(12)
V(1)–O(4)	2.335(3)	2.409(3)	O(2)–V(1)–N(1)	95.09(15)	95.01(13)
V(1)–N(1)	2.144(3)	2.131(3)	O(3)–V(1)–N(1)	92.15(12)	91.95(12)
V(1)–N(2)	2.186(3)	2.183(3)	O(1)–V(1)–N(1)	156.01(15)	157.09(12)
V(1)–V(2)	3.1122(7)	3.2307(7)	O(2)–V(1)–N(2)	95.67(13)	98.35(13)
V(2)–O(3)	2.302(3)	2.437(3)	O(3)–V(1)–N(2)	156.34(12)	152.95(12)
V(2)–O(4)	1.669(2)	1.663(2)	O(1)–V(1)–N(2)	86.26(12)	85.95(11)
V(2)–O(5)	1.927(3)	1.915(3)	N(1)–V(1)–N(2)	76.01(12)	76.47(12)
V(2)–O(6)	1.610(3)	1.623(3)	O(2)–V(1)–O(4)	171.43(12)	171.80(12)
V(2)–N(3)	2.126(3)	2.127(3)	O(3)–V(1)–O(4)	78.18(10)	77.48(10)
V(2)–N(4)	2.154(3)	2.171(3)	O(1)–V(1)–O(4)	83.90(11)	83.82(10)
			N(1)–V(1)–O(4)	77.07(12)	77.85(11)
			N(2)–V(1)–O(4)	79.22(10)	76.21(10)
			C(7)–N(2)–C(6)	119.6(3)	119.9(3)
			O(6)–V(2)–O(4)	106.43(14)	107.89(14)
			O(6)–V(2)–O(5)	100.80(13)	100.92(12)
			O(4)–V(2)–O(5)	99.96(12)	99.27(11)
			O(6)–V(2)–N(3)	93.13(14)	93.88(13)
			O(4)–V(2)–N(3)	91.57(12)	91.21(12)
			O(5)–V(2)–N(3)	158.51(14)	158.19(11)
			O(6)–V(2)–N(4)	98.94(13)	102.77(12)
			O(4)–V(2)–N(4)	152.59(13)	147.70(12)
			O(5)–V(2)–N(4)	85.02(12)	84.46(11)
			N(3)–V(2)–N(4)	76.65(12)	76.65(11)
			O(6)–V(2)–O(3)	171.07(13)	173.07(12)
			O(4)–V(2)–O(3)	79.34(10)	76.72(10)
			O(5)–V(2)–O(3)	84.61(11)	83.15(10)
			N(3)–V(2)–O(3)	79.75(11)	80.71(10)
			N(4)–V(2)–O(3)	74.29(11)	71.86(9)
			C(20)–N(4)–C(19)	119.2(3)	120.3(3)

Table S2 Structures of dinuclear V compounds with ligands acting as tridentate or tetradentate donors selected from the Cambridge Database.

Cambridge Database code	Core	Configuration	Angle V–O–V (°)	Oxidation state of V	Ligand acting as	Reference
ALADEW	$[V_2O_2(\mu_2\text{-OL})_2]$	Antiparallel-*anti*-coplanar	–	V-V	tetradentate	*J. Biol. Inorg. Chem.* **7**, 384 (2002)
AVNLAC	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*J. Chem. Soc., Chem. Commun.* 707 (1979)
BECCIV	$[V_2O_3]^{3+}$	Paralell-*syn*-angular	149.7	IV-V	tridentate	*Inorg. Chem.* **38**, 1982 (1999)
BEWDOX	$[V_2O_4]^{2+}$	Antiparallel (type A)-*anti*-coplanar	–	V-V	tridentate	*Chem. Eur. J.* **10**, 2301 (2004)
BIWCAL	$[V_2O_3]^{4+}$	*Twist*-angular	156	V-V	tridentate	*Inorg. Chim. Acta* **61**, 121 (1982)
BUPCEU	$[V_2O_3]^{3+}$	*Anti*-linear	179.5	IV-V	tridentate	*Inorg. Chem.* **22**, 1168 (1983)
DAGWIR	$[V_2O_3]^{3+}$	*Anti*-linear	164-169	IV-V	tetradentate	*Inorg. Chem.* **24**, 1052 (1985)
DEMKEM	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Acta Crystallogr., Sect. E* **62**, m1919 (2006)
DEQRUM	$[VO(\mu_2\text{-OR})_2VO]^{4+}$	*Anti*-orthogonal	–	V-V	tridentate	*Inorg. Chem.* **38**, 4303 (1999)
DOTQAE	$V_2O_2(OL)_2$	Antiparallel-*anti*-orthogonal	–	IV-IV	tetradentate	*J. Chem. Soc., Dalton Trans.* 1573 (2000)
DUMHUO	$[V_2O_3]^{4+}$	*Anti*-linear	180	V-V	tridentate	*Aust. J. Chem.* **39**, 1081 (1986)
EHILUC	$[VO(\mu_2\text{-OR})_2VO]^{4+}$	*Syn*-orthogonal	-	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 1813 (2003)
EJUCIC	$[V_2O_3]^{4+}$	*Twist*-angular	104.2	V-V	tridentate	*Eur. J. Org. Chem.* 2388 (2003)
FEKGUY	$[V_2O_3]^{2+}$	*Anti*-linear	180	IV-IV	tetradentate	*Chin. J. Inorg. Chem* **21**, 101 (2005)
FIQFOA	$[V_2O_3(H_2O)_2]^{4+}$	*Twist*-angular	151.5	V-V	tridentate	*Inorg. Chem. Commun.* **2**, 57 (1999)
GAVROL	$[VO(\mu_2\text{-OR})_2VO]^{4+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Acta Crystallogr., Sect. E* **61**, m2214 (2005)
HAKROA	$[V_2O_4]^{2+}$	Antiparallel (type C)-*anti*-coplanar	–	V-V	tridentate	*Inorg. Chem.* **32**, 3855 (1993)
HAZFUJ	$[V_2O_3]^{4+}$	*Twist*-angular	112.6	V-V	tridentate	*Z. Naturforsch., B: Chem. Sci.* **48**, 1848 (1993)
HAZFUJ01	$[V_2O_3]^{4+}$	*Twist*-angular	112.9	V-V	tridentate	*Bull. Chem. Soc. Jpn.* **73**, 357 (2000)
HENHIS	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Inorg. Chim. Acta* **359**, 4557 (2006)
HERCAI	$[V_2O_3]^{4+}$	*Twist*-angular	117.3	V-V	tridentate	*Polyhedron* **13**, 2495 (1994)
HOWWAR	$[V_2O_3]^{3+}$	Linear (polymer)	172.7	IV-V	tetradentate	*J. Chem. Soc., Dalton Trans.* 4437 (1999)
IFUSOR	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Z. Anorg. Allg. Chem.* **628**, 1140 (2002)
IQEPOJ	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Chin. J. Inorg. Chem.* **20**, 236 (2004)
JEGKUB	$[V_2O_3]^{4+}$	*Anti*-linear	180	V-V	tridentate	*Inorg. Chem.* **29**, 363 (1990)
JICLUC	$[V_2O_3]^{3+}$	Linear (polymer)	161.5	IV-V	tetradentate	*J. Chem. Soc., Dalton Trans.* 61 (1991)
JUYKET	$[V_2O_3]^{4+}$	*Twist*-angular	107.2	V-V	tridentate	*Z. Anorg. Allg. Chem.* **619**, 669 (1993)
KACRUB	$[V_2O_4]^{2+}$	Antiparallel (type A)-*Anti*-coplanar	–	V-V	tridentate	*Inorg. Chem.* **27**, 4657 (1988)
KERDUG	$[V_2O_3]^{4+}$	*Twist*-angular	116.2–141.3	V-V	tridentate	*Bull. Chem. Soc. Jpn.* **62**, 760 (1989)
KEJTUP	$[V_2O_2(\mu_2\text{-OL})_2]$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Inorg. Chem.* **45**, 2903 (2006)
KOHQED	$[V_2O_3]^{4+}$	*Twist*-angular	112.9	V-V	tridentate	*Bull. Chem. Soc. Jpn.* **73**, 357 (2000)
LAGGEG	$[V_2O_3]^{2+}$	*Anti*-linear	180	IV-IV	tetradentate	*Polyhedron* **23**, 1975 (2004)
LAVTIL	$[V_2O_3]^{4+}$	*Anti*-linear	160.8	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 2857 (1993)
LIJDAJ	$[V_2O_4]^{2+}$	Antiparallel-*Anti*-coplanar	–	V-V	tridentate	*Inorg. Chem.* **33**, 4669 (1994)
MENLIA	$[V_2O_3]^{4+}$	*Anti*-angular	128.3	V-V	tridentate	*Eur. J. Inorg. Chem.* 1645 (2000)
MIZCON	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **41**, 2243 (2002)
ODUBOE	$[V_2O_3]^{4+}$	*Twist*-angular	112.1	V-V	tridentate	*Inorg. Chem.* **41**, 1684 (2002)
PAQVEI	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **37**, 64 (1998)
PECJAI	$[V_2O_2(\mu_2\text{-OL})_2]$	Antiparallel-*anti*-orthogonal	–	V-V	tetradentate	*J. Chem. Soc., Dalton Trans.* 2383 (1998)
PEHYEG	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Chin. J. Struct. Chem.* **12**, 79 (1993)
PERGAV	$[V_2O_4]^{2+}$	Antiparallel-*Anti*-coplanar	–	V-V	tridentate	*Polyhedron* **25**, 2809 (2006)
PIKTIN	$[V_2O_3]^{4+}$	Twist	157.8	V-V	tridentate	*Inorg. Chem.* **46**, 5483 (2007)

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QAYWES	$[VO(\mu_2\text{-}OR)_2VO]^{4+}$	Antiparallel (type A)-*anti*-coplanar	–	V-V	tridentate	*Polyhedron* **19**, 2003 (2000)
QUDGIF	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*J. Chem. Cryst.* **30**, 329 (2000)
RETZUL	$[V_2O_3]^{3+}$	*Twist*-angular	113.2	IV-V	tridentate	*Inorg. Chem.* **36**, 59 (1997)
RIZFAH	$[V_2O_4]^{2+}$	Antiparallel (type C)-*anti*-coplanar	–	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 917 (1997)
ROCKID	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **36**, 1657 (1997)
ROQBUU	$[V_2O_3]^{3+}$	*Syn*-angular	143.9	IV-V	tridentate	*Inorg. Chem.* **36**, 4954 (1997)
SOCMIG	$[V_2O_2]^{+}$	Linear (polymer)	162.2, 180	IV-V	tetradentate	*J. Chem. Soc., Chem. Commun.* 827 (1991)
TABMOZ	$[V_2O_3]^{3+}$	*Syn*-angular	135.1	IV-V	tridentate	*Chem.—Eur. J.* **9**, 1805 (2003)
TAWZAS	$[V_2O_3(H_2O)]^{4+}$	*Twist*-angular	118	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 1989 (1996)
TICKAS	$[VO(\mu_2\text{-}OR)_2VO]^{2+}$	*Anti*-orthogonal	–	IV-IV	tridentate	*Inorg. Chim. Acta* **360**, 2681 (2007)
TIFTEI	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Polyhedron* **26**, 2713 (2007)
TOZRIJ	$[V_2O_3]^{4+}$	*Twist*-angular	109.3	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 3865 (1996)
TUNXIJ	$[V_2O_2]^{+}$	Linear	162.7, 166.6	III-V	tetradentate	*Inorg. Chem.* **35**, 6634 (1996)
VAYMIR	$[VO(\mu_2\text{-}OR)_2VO]^{4+}$	Antiparallel-*anti*-coplanar	–	IV-IV	tridentate	*Sci. Sin., Ser. B (Engl. Ed.)* **31**, 781 (1988)
VEBNEW	$[V_2O_3]^{4+}$	*Syn*-linear	167.9	V-V	tridentate	*Inorg. Chem.* **45**, 1260 (2006)
WIHQEJ	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Inorg. Chem.* **39**, 3252 (2000)
XIVJUH	$[VO(\mu_2\text{-}OR)_2VO]^{4+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*J. Coord. Chem.* **51**, 55 (2000)
XUMHUI	$[V_2O_3]^{3+}$	*Anti*-linear	170.9	IV-V	tridentate	*J. Chem. Soc., Dalton Trans.* 4407 (2002)
YAZGIP	$[V_2O_4]^{2+}$	Antiparallel-*anti*-coplanar	–	V-V	tridentate	*Inorg. Chem.* **32**, 6119 (1993)
ZUFJOZ	$[V_2O_3]^{3+}$	*Anti*-linear	165.4	IV-IV	tetradentate	*Inorg. Chim. Acta* **240**, 217 (1995)
ZUFXIH	$[V_2O_2(\mu_2\text{-}OL)_2]$	Antiparallel-*anti*-coplanar	–	IV-IV	tetradentate	*Angew. Chem., Int. Ed. Engl.* **35**, 627 (1996)

Table S3 Dinuclear V compounds with ligands acting as tetradentate donors.

Cambridge Database code	Core	Configuration	Angle V-O-V(°)	Oxidation state of V	Ligand acting as	Reference
AVNLAC	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*J. Chem. Soc., Chem. Commun.* 707 (1979)
BUPCEU	$[V_2O_3]^{3+}$	*Anti*-linear	179.5	IV-V	tetradentate	*Inorg. Chem.* **22**, 1168 (1983)
DAGWIR	$[V_2O_3]^{3+}$	*Anti*-linear	164–169	IV-V	tetradentate	*Inorg. Chem.* **24**, 1052 (1985)
FEKGUY	$[V_2O_3]^{2+}$	*Anti*-linear	180	IV-IV	tetradentate	*Chin. J. Inorg. Chem.* **21**, 101 (2005)
HOWWAR	$[V_2O_3]^{3+}$	Linear (polymer)	172.7	IV-V	tetradentate	*J. Chem. Soc., Dalton Trans.* 4437 (1999)
JICLUC	$[V_2O_3]^{3+}$	Linear (polymer)	161.5	IV-V	tetradentate	*J. Chem. Soc. Dalton Trans.* 61 (1991)
LAGGEG	$[V_2O_3]^{2+}$	*Anti*-linear	180	IV-IV	tetradentate	*Polyhedron* **23**, 1975 (2004)
MIZCON	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **41**, 2243 (2002)*
PAQVEI	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **37**, 64 (1998)*
PEHYEG	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Chinese J. Struct. Chem.* **12**, 79 (1993)
ROCKID	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **36**, 1657 (1997)
SOCMIG	$[V_2O_2]^{+}$	Linear (polymer)	162.2, 180	IV-V	tetradentate	*J. Chem. Soc., Chem. Commun.* 827 (1991)
ZUFJOZ	$[V_2O_3]^{3+}$	*Anti*-linear	165.4	IV-V	tetradentate	*Inorg. Chim. Acta* **240**, 217 (1995)*

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Table S4 Dinuclear V cores with *twist*-angular configuration.

Cambridge Database code	Core	Configuration	Angle V–O–V(°)	Oxidation state of V	Ligand acting as	Reference
BIWCAL	$[V_2O_3]^{4+}$	*Twist*-angular	156	V-V	tridentate	*Inorg. Chim. Acta* **61**, 121 (1982)
EJUCIC	$[V_2O_3]^{4+}$	*Twist*-angular	104.2	V-V	tridentate	*Eur. J. Org. Chem.* 2388 (2003)
FIQFOA	$[V_2O_3(H_2O)_2]^{4+}$	*Twist*-angular	151.5	V-V	tridentate	*Inorg. Chem. Commun.* **2**, 57 (1999)
HAZFUJ	$[V_2O_3]^{4+}$	*Twist*-angular	112.6	V-V	tridentate	*Z. Naturforsch., B: Chem. Sci.* **48**, 1848 (1993)
HAZFUJ01	$[V_2O_3]^{4+}$	*Twist*-angular	112.9	V-V	tridentate	*Bull. Chem. Soc. Jpn.* **73**, 357 (2000)
HERCAI	$[V_2O_3]^{4+}$	*Twist*-angular	117.3	V-V	tridentate	*Polyhedron* **13**, 2495 (1994)
JUYKET	$[V_2O_3]^{4+}$	*Twist*-angular	107.2	V-V	tridentate	*Z. Anorg. Allg. Chem.* **619**, 669 (1993)
KERDUG	$[V_2O_3]^{4+}$	*Twist*-angular	116.2–141.3	V-V	tridentate	*Bull. Chem. Soc. Jpn.* **62**, 760 (1989)
KOHQED	$[V_2O_3]^{4+}$	*Twist*-angular	112.9	V-V	tridentate	*Bull. Chem. Soc. Jpn.* **73**, 357 (2000)
ODUBOE	$[V_2O_3]^{4+}$	*Twist*-angular	112.1	V-V	tridentate	*Inorg. Chem.* **41**, 1684 (2002)
PIKTIN	$[V_2O_3]^{4+}$	Twist	157.8	V-V	tridentate	*Inorg. Chem.* **46**, 5483 (2007)
RETZUL	$[V_2O_3]^{3+}$	*Twist*-angular	113.2	IV-V	tridentate	*Inorg. Chem.* **36**, 59 (1997)
TAWZAS	$[V_2O_3(H_2O)]^{4+}$	*Twist*-angular	118	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 1989 (1996)
TOZRIJ	$[V_2O_3]^{4+}$	*Twist*-angular	109.3	V-V	tridentate	*J. Chem. Soc., Dalton Trans.* 3865 (1996)

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Table S5 Mixed-valence dinuclear V complexes with the $[V_2O_3]^{3+}$ core.

Cambridge Database code	Core	Configuration	Angle V–O–V(°)	Oxidation state of V	Ligand acting as	Reference
AVNLAC	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*J. Chem. Soc., Chem. Commun.* 707 (1979)
BECCIV[a]	$[V_2O_3]^{3+}$	*Syn*-angular	149.7	IV-V	tridentate	*Inorg.Chem.* **38**, 1982 (1999)
DAGWIR	$[V_2O_3]^{3+}$	*Anti*-linear	164–169	IV-V	tetradentate	*Inorg.Chem.* **24**, 1052 (1985)
HOWWAR	$[V_2O_3]^{3+}$	Linear (polymer)	172.7	IV-V	tetradentate	*J. Chem. Soc.,Dalton Trans.* 4437 (1999)
JICLUC	$[V_2O_3]^{3+}$	Linear (polymer)	161.5	IV-V	tetradentate	*J. Chem. Soc., Dalton Trans.* 61 (1991)
MIZCON	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **41**, 2243 (2002)[a]
PAQVEI	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **37**, 64 (1998)[a]
PEHYEG	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Chin. J. Struct. Chem.* **12**, 79 (1993)
RETZUL[b]	$[V_2O_3]^{3+}$	*Twist*-angular	113.2	IV-V	tridentate	*Inorg. Chem.* **36**, 59 (1997)
ROCKID	$[V_2O_3]^{3+}$	*Anti*-linear	180	IV-V	tetradentate	*Inorg. Chem.* **36**, 1657 (1997)
ROQBUU[a]	$[V_2O_3]^{3+}$	*Syn*-angular	143.9	IV-V	tridentate	*Inorg. Chem.* **36**, 4954 (1997)
SOCMIG	$[V_2O_2]^{+}$	Linear (polymer)	162.2, 180	IV-V	tetradentate	*J. Chem. Soc., Chem. Commun.* 827 (1991)
TABMOZ[a]	$[V_2O_3]^{3+}$	*Syn*-angular	135.1	IV-V	tridentate	*Chem. Eur. J.* **9**, 1805 (2003)
XUMHUI[c]	$[V_2O_3]^{3+}$	*Anti*-linear	170.9	IV-V	tridentate	*J. Chem. Soc., Dalton Trans.* 4407 (2002)

[a]The compound contains sulfur donor atoms.

[b]The complex was generated in solution by electroreduction at constant potential of the corresponding $[V^{V}_2O_3]^{4+}$ congener.

[c]The compound contains Na^+ as counterion in the crystal structure (it was obtained from a sodium acetate-containing solution).