

Supplementary Information

Table S1 Crystal and structure refinement data^[a] of compound **11** ($[\text{V}^{\text{V}}\text{O}\{\text{pyr}(S,S\text{-chen})\}_2(\mu\text{-O})_2\cdot 2(\text{CH}_3)_2\text{NCHO}]$).

11	
Formula	$\text{C}_{34}\text{H}_{58}\text{N}_8\text{O}_{10}\text{V}_2$
M_r	840.76
T [K]	100(2)
λ , Å [Mo, K_α]	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a [Å]	8.6992(10)
b [Å]	12.7434(14)
c [Å]	17.5411(19)
α [°]	90
β [°]	94.045(3)
γ [°]	90
Z	2
Volume [Å ³]	1939.7(4)
ρ_{calcd} [gcm ⁻³]	1.439
μ mm ⁻¹	0.547
Reflections measured	17853
Independent reflections ^[b]	6053
R(int)	0.0684
Goodness-of-fit on F^2	1.038
R_1 ^[c]	0.0626
wR_2 (all data) ^[c]	0.1732

[a] All structures were solved and refined using SHELXS Program for Crystal Structure Determination [27] [b] $I > 2\sigma(I)$

[c] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(F_o^4)]\}^{1/2}$

Characterization of the ligands and vanadium complexes

Table S2 – Assignment of selected IR frequencies (cm^{-1}) and UV-Vis and CD bands (in DMSO) for the ligands and their vanadium complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}-\text{H})$	$\nu(\text{V}=\text{O})$	UV-vis $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	CD $\lambda_{\text{max}}/\text{nm}$ ($\text{mol CD}/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)
pyr(<i>R,R</i> -chen) 1	1628	1291			244 (1250), 312 (1090), 392 (265) ^b	275 (3.03), 310 (-4.12), 356 (-4.01), 409 (sh, -0.39)
pyr(<i>R,R</i> -dpen) 2	1626	1291			258 (1950), 340 (698), 418 (687)	277 (-2.32), 305 (2.64), 346 (sh, 1.39)
pyr(<i>R,R</i> -chan) 3		1298	a		218 (2280), 250 (589), 296 (710), 324 (915) ^b	256 (1.37), 286 (-0.28), 293 (0.23), 323 (-2.30), 350 (0.076) ^b
pyr(<i>S,S</i> -dpan) 4		1290	a		210 (2680), 246 (sh, 509), 292 (1030) 324 (583) ^b	236 (12.1), 274 (-1.93), 309 (-3.29), 327 (-2.99) ^b
$\text{V}^{\text{V}}\text{O}[\text{pyr}(\text{S,S}-\text{chen})]$ 5	1626	1266		888	270 (sh, 14 850), 380 (7700), 574 (131), 738 (sh, 55)	281 (-3.3), 304 (sh, -2.3), 373 (1.3), 413 (-1.5)
$\text{V}^{\text{IV}}\text{O}[\text{pyr}(\text{S,S}-\text{dpen})]$ 6	1625	1264		990	280 (sh, 11 040), 386 (6180), 586 (95), 746 (sh, 48)	275 (3.2), 393 (-1.7)
$\text{V}^{\text{IV}}\text{O}[\text{pyr}(\text{S,S}-\text{chan})]$ 7 ^c		1248	3228	885	298 (16 850), 506 (sh, 250), 770 (125)	
$\text{V}^{\text{IV}}\text{O}[\text{pyr}(\text{S,S}-\text{dpan})]$ 8 ^c		1288	a	930 or 891	294 (20 140), 560 (sh, 135), 800 (51)	
$\{\text{V}^{\text{V}}\text{O}[\text{pyr}(\text{S,S}-\text{chan})]\}_2(\mu\text{-O})$ ₉		1289		931	284 (10 943), 382 (2215), 522 (497)	254 (0.56), 291 (-0.20), 390 (-0.034)
$\{\text{V}^{\text{V}}\text{O}[\text{pyr}(\text{S,S}-\text{dpan})]\}_2(\mu\text{-O})$ ₁₀		1291		923	288 (12 588), 400 (2280), 510 (sh, 1536)	282 (6.15), 301 (5.53), 325 (-2.38), 406 (2.11), 513 (-4.10)

^a Under broad band, ^b H_2O , ^c the solutions change with time, the data presented is after addition of excess $\text{Na}_2\text{S}_2\text{O}_4$.

Circular dichroism

In the CD spectra the salan ligands show Cotton effects with lower rotational strength than the salen parent compounds. This can be explained by the fact that single bonds are not efficient in transmitting chirality and the chromophores are far from the chiral centres of the molecules; moreover, the higher flexibility of the salan compounds when compared to the salen also allows the presence of other conformers in equilibrium. In the salen compounds the extended resonance throughout the imine bonds allows a relatively efficient transmission of chirality to the chromophores and the CD signals are much more intense.

Compounds **1** and **2** present a band at *ca.* 350 nm, which is assigned essentially to the lower energy $\pi \rightarrow \pi^*$ transition of the imine group, whereas the wing shaped Cotton effects at higher energy are the result of exciton coupled $\pi \rightarrow \pi^*$ transitions, which are of opposite signs in these ligands, indicating different conformations in the spatial arrangement of the diamines: **1** shows negative chirality, $\Delta\lambda$ and **2** positive chirality, $\Lambda\delta$.

The CD spectrum of **3** shows a negative CD band at 323 nm (one of the λ_{max} of the absorption spectrum). The band, which in the absorption spectrum appears at 296 nm, is split in two low intensity CD bands with opposite signals, centred at 290 nm. Below these there are other high-energy bands due to aromatic transitions. Compound **4** also shows a negative CD signal for the lower energy $\pi \rightarrow \pi^*$ transition, but the next transition seems to be split into two CD bands of negative/positive signals, although the superposition of the bands does not allow to clearly see the positive band. There is no data in the literature about chiral salicylaldamine CD spectra and therefore we cannot go further in comparison with other data.

The CD spectra of the V^{IV}O-salen type complexes have been studied and reported [1]. For V-salen complexes the vicinal effect is not important and usually the signs of the Cotton effects are determined by the conformation of the central chelate ring and the configuration of the pseudotetrahedral arrangement of the chelate ligand donor atoms. The signal of the exciton coupling can be used to predict the conformation of the chelate ring around the metal ion. For the present complexes the exciton theory requires that the

1. M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, R.D. Gillard. *Gazz. Chim. Ital.* **102**, 853 (1972).

imine transition moment vectors form a left-handed helix about the pseudo- C_2 axis of the molecules, when the positive component of the CD couplet occurs at lower energy, originating a tetrahedral arrangement of Λ configuration [2]. In complex **5** the $\pi \rightarrow \pi^*$ transition associated with the C=N bond is shifted to lower energy (when compared to the parent ligand, see Table 2) producing a wing shaped splitting with two components. The exciton couplet is centred at 392 nm and the low energy CD couplet has the same signal as complex VO[sal(chen)] (at 413 nm, negative) [3] and therefore both complexes should have the same configuration, Δ . For complex **6** the situation is not so clear. The 1st band observed in the UV range ($\pi \rightarrow \pi^*$ transition associated with the imine bond) has almost the same λ_{max} in the electronic absorption and the CD spectra (387 vs. 393 nm). Therefore, no exciton interaction is observed.

2. N. R. Sangeetha, S. Pal. *Bull. Chem. Soc. Jpn.* **73**, 357 (2000).

3. P. Adão, I. Correia, R. T. Henriques, M. Kuznetsov, F. Avecilla, M. R. Maurya, U. Kumar, J. Costa Pessoa. Submitted to *Inorg. Chem.*

Magnetic properties

The magnetic susceptibilities, χ , of the vanadium(IV) complexes **7** and **8** were measured by the Faraday method in the temperature range of 3–300 K. Data were corrected for the diamagnetic contribution using the Pascal constants [4]. The magnetic susceptibility of both complexes fit well the Curie-Weiss law with a temperature independent paramagnetism term [$\chi = C/(T-\theta) + \text{TIP}$]. Fig. S1 shows the variation of the magnetic susceptibility and effective magnetic moment (μ_{eff}) with temperature and the parameters obtained from the fitting can be found in Table S3. The strength of antiferromagnetic coupling is minimal, as suggested by the Weiss constants, which are near zero. The effective magnetic moment per vanadium atom determined for both complexes at 300 K is 1.8 B.M., close to the spin-only value of 1.73 B.M. expected for $d^1 \text{V}^{\text{IV}}$ -containing systems. The low $\nu(\text{V}=\text{O})$ values obtained for both complexes indicate some interaction of the $\text{V}=\text{O}$ units, possibly of the type $\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots\text{V}=\text{O}$. However, the magnetic measurements indicate that these interactions are not strong enough to change the μ_{eff} values significantly, the compounds behaving as monomeric units as far as magnetic interactions are concerned.

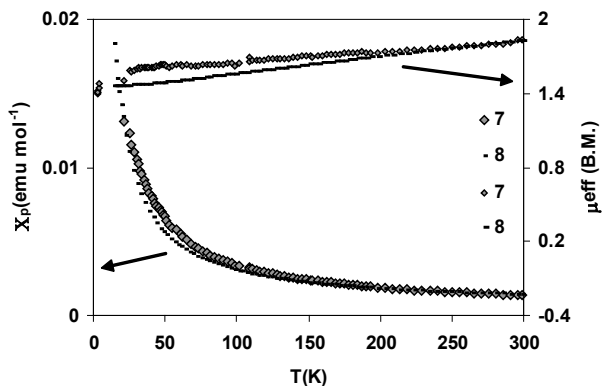


Fig. S1 Variation of the magnetic susceptibility and μ_{eff} of complexes **7** and **8** with temperature.

4 . P. W. Selwood. *Magnetochemistry*, Interscience, New York 1956, p. 78.

Table S3 – Parameters obtained from the fitting of the magnetic susceptibility with the Curie Weiss law with TIP.

Magnetic properties			
Complex	C (emu K mol⁻¹)	θ (K)	TIP (emu mol⁻¹)
7	0.326	-1.03	2.1 x 10 ⁻⁴
8	0.243	0.88	5.7 x 10 ⁻⁴

Crystal structure of $\{[V^V O\{pyr(S,S\text{-}chen)\}]_2(\mu\text{-}O)_2 \cdot 2(CH_3)_2NCHO\}$ **11**

Besides the interactions between the μ -oxo groups and the vanadium atoms, there are strong hydrogen bonds between i) the phenolate-O atoms and the primary amine-N atoms [O(1) \cdots N(4) 2.862(7) Å and O(5) \cdots N(1) 2.938(7) Å]; ii) one of μ -oxo groups and the secondary amine atom [O(3) \cdots N(5) 2.672(8) Å] and iii) the alcoholate-O atoms and the pyridinic nitrogens [O(7) \cdots N(3) 2.769(7)Å and O(8) \cdots N(6) 2.739(8) Å]. There is an extended network of close contacts in the three-dimensional crystal structure that involves mainly the DMF molecules and the oxo groups of adjacent molecules.

Table S4 Intra- and inter-molecular hydrogen bonds (Å, °) and C-H \cdots Cl contacts in **11** ($[V^V O\{pyr(S,S\text{-}chen)\}]_2(\mu\text{-}O)_2 \cdot 2(CH_3)_2NCHO$).

$\{[V^V O\{pyr(1S,2S\text{-}chen)\}]_2(\mu\text{-}O)_2 \cdot 2(CH_3)_2NCOH\}$ 11				
D-H \cdots A	D-H (Å)	H \cdots A(Å)	D \cdots A(Å)	D-H \cdots A (°)
N1-H1NB...O2S	0.90	2.49	3.133(9)	128.6
N1-H1NA...O5	0.90	2.17	2.938(7)	143.1
N2-H2N...O6	0.91	2.23	3.095(7)	158.7
N4-H4NB...O1	0.90	2.07	2.862(7)	146.1
N4-H4NB...O1S	0.90	2.63	3.129(8)	116.2
N5-H5...O3	0.91	2.11	2.672(8)	118.7
O7-H7...N3	0.82	1.96	2.769(7)	169.1
O8-H8...N6	0.82	2.02	2.739(8)	146.9