



# Ferromagnetic oxovanadium(IV) complexes chelated with tetrahalosalen ligands

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## ABSTRACT

Five oxovanadium(IV) complexes [VO(X<sub>4</sub>salen)] have been prepared and characterized, where each benzene ring was substituted with two halogen atoms in salen (H<sub>2</sub>salen = *N,N'*-disalicylideneethylenediamine). The X-ray diffraction study on 3,3',5,5'-tetrachloro-, 3,3',5,5'-tetrabromo-, and 4,4',6,6'-tetrachlorosalen derivatives clarified their polymeric structure with the (–V=O–)<sub>n</sub> repeating unit. The interatomic V...V distances are 3.710(3), 3.695(3), and 3.749(3) Å, respectively, being shorter than that of known [VO(salpn)] (3.83 Å; H<sub>2</sub>salpn = *N,N'*-disalicylidenepropylenediamine). The exchange coupling parameters (*J*) were determined by fitting the magnetic susceptibility data to the one-dimensional ferromagnetic model, giving 2*J*/*k*<sub>B</sub> = 8.2–16 K, which are the largest in the [VO(salen)] and [VO(salpn)] family.

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## 1. Introduction

Various self-assemblies are formed in the coordination chemistry of vanadium which exhibits a variety of oxidation states, and vanadium(III) compounds have been investigated for single-molecule magnets and related magnetic materials [1,2]. Vanadium chemistry has also attracted attention due to its interesting structural features including biological relevance [3]. Whereas the magneto-structural correlation in copper(II) complexes (3d<sup>9</sup>; *S* = 1/2) with various bridging ligands are intensively studied [4–6], relatively little is known about complexes with vanadium(IV) (3d<sup>1</sup>; *S* = 1/2) [7]. Oxovanadium(IV) complexes containing tetradentate Schiff bases have been the subject of various studies [8–11], where the Schiff base ligands are derived from diamines and salicylaldehyde derivatives.

Most oxovanadium(IV) complexes with a tetradentate Schiff-base ligand like salen (H<sub>2</sub>salen stands for *N,N'*-disalicylideneethylenediamine) are green and have monomeric structures with square-pyramidal coordination geometry [12]. On the other hand, orange complexes having polynuclear linear chain structures (–V=O–)<sub>n</sub> are observed in the solid state for the Schiff base–oxovanadium(IV) complexes which have a six-membered N–N chelate ring (namely, [VO(salpn)]); H<sub>2</sub>salpn stands for *N,N'*-disalicylidenepropylenediamine [13] or electron-withdrawing substituents at salicylaldehyde moieties [14]. The temperature dependence of the magnetic susceptibility of linear polynuclear [VO(salpn)] was reported by Drake et al. [15]. Ferromagnetic exchange interaction was observed between the molecules in the chains. Further studies

on the magnetic properties of polynuclear oxovanadium(IV) complexes have not been developed systematically. In the present study, we introduced two halogen atoms onto the salen benzene rings in [VO(salen)], because multi-halogenation would give rise to tighter packing of the molecular crystals. Actually, we have succeeded in the preparation of ferromagnetic derivatives from the [VO(salen)] family, and furthermore the magnitude of the ferromagnetic couplings has been improved compared with those of [VO(salpn)] and related compounds. We will describe the preparation, spectral and structural characterization, and magnetic properties on the tetrahalo-[VO(salen)] derivatives.

## 2. Results and discussion

### 2.1. Synthesis and IR-spectroscopic characterization

We have prepared and characterized several oxovanadium(IV) complexes of tetradentate Schiff base ligands. A structural representation of the complexes studied and their abbreviations are given in Fig. 1, where X<sub>4</sub>salen stands for *N,N'*-ethylenebis(3,5-dihalosalicylideneamine) (X = F, Cl, Br, and I) and iX<sub>4</sub>salen for its isomeric *N,N'*-ethylenebis(4,6-dihalosalicylideneamine) (X = Cl). H<sub>2</sub>Cl<sub>4</sub>salen, H<sub>2</sub>Br<sub>4</sub>salen, and H<sub>2</sub>I<sub>4</sub>salen are known [12,16], and other new compounds are similarly prepared and characterized. Though very fine powdery samples were easily obtained in a conventional manner, the preparation of single crystals suitable for the X-ray crystallographic analysis is considerably difficult. A slow diffusion method was applied by contacting two dilute solutions containing the ligand and pyridine (dimethyl sulfoxide) and oxovanadium(IV) sulfate (methanol) for a few weeks. When the solvent was wet, water-capped monomeric compounds [VO(X<sub>4</sub>salen)(H<sub>2</sub>O)] were sometimes separated.

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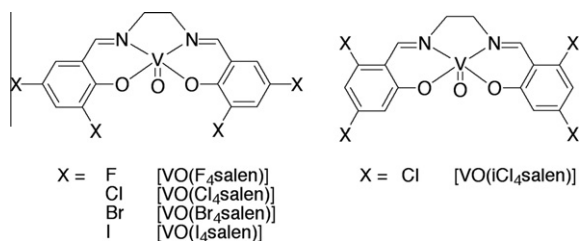


Fig. 1. Molecular structures and abbreviations.

All of the oxovanadium(IV) complexes investigated here have orange to brown color and the IR  $\text{V}=\text{O}$  stretching bands in  $858\text{--}872\text{ cm}^{-1}$ . This finding indicates that they are assigned to the distorted octahedral coordination forming a linear chain polymer  $(-\text{V}=\text{O}-)_n$  in the solid state [16,17]. On the other hand, the unsubstituted Schiff-base derivative, namely  $[\text{VO}(\text{salen})]$ , gave a green compound with a monomeric square-pyramidal coordination, as reproduction of many previous reports [18]. Pasquali and co-workers reported the somewhat low  $\text{V}=\text{O}$  stretching frequency ( $885\text{ cm}^{-1}$ ) for bis[*N*-(4-chlorophenyl)salicylideneaminato]oxovanadium(IV) [19], and Hamilton [20] and Mathew et al. [13] clarified the low  $\text{V}=\text{O}$  stretching frequency indicates the weakening of the  $\text{V}=\text{O}$  bond by the oxygen bridging in the oxovanadium(IV) complexes. Thus, the color and IR absorption bands became a fingerprint of chain and monomeric complexes; IR spectra of these complexes show the  $\text{V}=\text{O}$  stretching bands around  $960\text{--}990\text{ cm}^{-1}$  for monomers and around  $850\text{--}880\text{ cm}^{-1}$  for polymers [17]. Yoshioka et al. reported the pressure-induced solid–solid phase transition on the derivative having 5,5'-dinitrosalen [14b,21], as a useful application of this fingerprint. In our compounds, such interconversion was not observed.

## 2.2. Crystallographic analysis

The polymeric structures were unequivocally evidenced from the single-crystal X-ray diffraction study (Table 1 and Fig. 2). Unfortunately,  $[\text{VO}(\text{F}_4\text{salen})]$  and  $[\text{VO}(\text{I}_4\text{salen})]$  gave very fine needles, which are unsuitable for the single-crystal X-ray diffraction analysis. Two compounds  $[\text{VO}(\text{Cl}_4\text{salen})]$  and  $[\text{VO}(\text{Br}_4\text{salen})]$  are isomorphous in the orthorhombic space group *Pnma*. As Fig. 2 shows, the molecules construct a one-dimensional structure. The *a* cell length is approximately related with a twice of the  $\text{V}\cdots\text{V}$  distance. The important geometrical parameters are summarized in Table 2. There is one crystallographically independent V ion, and accordingly the  $\text{V}\cdots\text{V}$  relation is unique. The interatomic  $\text{V}\cdots\text{V}$  distances in  $[\text{VO}(\text{Cl}_4\text{salen})]$  and  $[\text{VO}(\text{Br}_4\text{salen})]$  were  $3.710(3)$  and  $3.695(3)\text{ \AA}$ , respectively (Fig. 2), which are shorter than that of the known  $[\text{VO}(\text{salpn})]$  ( $3.83\text{ \AA}$ ) exhibiting ferromagnetic coupling.

The vanadium(IV) ion has a basically five-coordinated square pyramid structure, and the vanadium ion is located slightly above the  $\text{N}_2\text{O}_2$  basal plane toward the oxo cap. Accordingly the molecule has a V-shape. A half of a molecule is crystallographically independent. The molecules are stacked along the crystallographic *a*-axis, which is favorable to the Coulombic attraction between the neighboring V ion and oxo O atoms. The ethylene groups are located alternately to avoid the steric congestion (Fig. 2a). As a result, the halogen atoms at the 5- and 5'-positions ( $\text{Cl}2$  and  $\text{Br}2$ ) are also located alternately and comparably apart. The interatomic distances are  $4.268(3)\text{ \AA}$  for  $\text{Cl}2\cdots\text{Cl}2^*$  in  $[\text{VO}(\text{Cl}_4\text{salen})]$  and  $4.222(2)\text{ \AA}$  for  $\text{Br}2\cdots\text{Br}2^*$  in  $[\text{VO}(\text{Br}_4\text{salen})]$ , which are somewhat longer than the sum of the van der Waals radii ( $3.60$  and  $3.90\text{ \AA}$ , respectively) [22]. As the side-views show (Fig. 2b and c), the polymer  $(-\text{V}=\text{O}-)_n$  backbone is shown with the close atomic contacts between the V and O atoms in an approximately collinear manner.

Table 1  
Selected crystallographic data.

Compounds	$[\text{VO}(\text{Cl}_4\text{salen})]$	$[\text{VO}(\text{Br}_4\text{salen})]$	$[\text{VO}(\text{iCl}_4\text{salen})]$
Formula	$\text{C}_{16}\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_3\text{V}$	$\text{C}_{16}\text{H}_{10}\text{Br}_4\text{N}_2\text{O}_3\text{V}$	$\text{C}_{16}\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_3\text{V}$
Formula weight	471.02	648.82	471.02
Habit	orange needle	orange needle	orange needle
Dimension ( $\text{mm}^3$ )	$0.23 \times 0.03 \times 0.03$	$0.78 \times 0.07 \times 0.07$	$0.24 \times 0.04 \times 0.04$
<i>T</i> (K)	90	90	90
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pbca</i>
<i>a</i> ( $\text{\AA}$ )	7.413(4)	7.383(4)	16.526(3)
<i>b</i> ( $\text{\AA}$ )	25.005(14)	25.401(12)	7.4922(12)
<i>c</i> ( $\text{\AA}$ )	9.696(8)	10.021(6)	27.675(4)
<i>V</i> ( $\text{\AA}^3$ )	1797(2)	1879.1(17)	3426.6(10)
<i>Z</i>	4	4	8
<i>D</i> <sub>calc.</sub> ( $\text{g cm}^{-3}$ )	1.741	2.293	1.826
Unique data	2108	2175	3906
$\mu$ ( $\text{Mo K}\alpha$ ) ( $\text{mm}^{-1}$ )	1.165	9.078	1.222
<i>R</i> ( $F$ ) <sup>a</sup> ( $I > 2\sigma(I)$ )	0.0538	0.0625	0.0734
<i>R</i> <sub>w</sub> ( $F^2$ ) <sup>b</sup> (all data)	0.1203	0.0691	0.0963

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

The  $\text{V}1\text{--O}1^*$  distances are very short,  $2.114(5)$  and  $2.086(6)\text{ \AA}$  for  $[\text{VO}(\text{Cl}_4\text{salen})]$  and  $[\text{VO}(\text{Br}_4\text{salen})]$ , respectively, which correspond to 60% of the sum of the van der Waals radii ( $3.52\text{ \AA}$ ) [22].

The crystal structure of  $[\text{VO}(\text{iCl}_4\text{salen})]$  is shown in Fig. 2d and e, as top and side views of a chain. The chain runs along the crystallographic *b*-axis. A crystallographic independent unit is a whole molecule. Although the vanadium(IV) ion favors a five-coordinated square pyramid structure, two salen wings are arranged to be parallel in contrast to the results on the 3,3',5,5'-derivatives. The vanadium position is disordered with the optimized occupancy factors of 0.67/0.33 for  $\text{V}1/\text{V}2$ . Accordingly, the oxygen position would also be disordered, but a unique oxygen position was characterized in the parameter refinement. The  $\text{V}1\text{--O}1^\dagger$  distance ( $2.219(4)\text{ \AA}$ ) corresponds to 63% of the sum of the van der Waals radii. A top view is approximately similar to those of the 3,3',5,5'-derivatives, but a half portion is arranged to be slightly slipped off in a zigzag manner. The nearest  $\text{C}1\cdots\text{C}1$  distance is  $3.755(2)\text{ \AA}$  ( $\text{Cl}2\cdots\text{Cl}1^\dagger$ ), which is slightly longer than the sum of the van der Waals radii ( $3.60\text{ \AA}$ ) [22].

A preliminary crystallographic analysis on  $[\text{VO}(\text{I}_4\text{salen})]$  ( $R(F)$  ( $I > 2\sigma(I)$ ) = ca. 0.14) indicates that it crystallizes in a space group orthorhombic *Pna*<sub>2</sub>1 with  $a = 21.014(3)$ ,  $b = 26.515(4)$ ,  $c = 7.4836(12)\text{ \AA}$ , and  $V = 4169.8(11)\text{ \AA}^3$ . There are two independent molecules in a unit cell, and the  $\text{V}\cdots\text{V}$  distances are  $3.666(6)$  and  $3.821(6)\text{ \AA}$ .

In crystal engineering, Desiraju and co-workers have proposed the "dichloro rule" [23,24]. The crystal packing would be improved when the at least two halogen atoms are introduced to a molecule. Usually, this effect is attributed to possible halogen–halogen contacts [25]. In the present compounds, however, there is no appreciable halogen–halogen contact. We have also found a ferromagnetic compound using  $\text{F}_4\text{salen}$ , and  $\text{F}\cdots\text{F}$  contacts [26] can hardly be operative as an attractive interaction. Contrary to our initial expectation, the driving force of the crystal formation suitable for ferromagnetic  $\text{V}\cdots\text{V}$  couplings cannot be explained in terms of the "dichloro rule". Weak hydrogen bonds between halogen and hydrogen are found in the columnar direction. Furthermore, halogen atoms are electron-withdrawing, bringing about electron deficient aromatic rings in salen. As Tsuchimoto and Yoshioka suggested, this factor is favorable for the columnar molecular arrangement showing ferromagnetic couplings [14b].

## 2.3. Magnetic properties

The magnetic susceptibilities of polycrystalline samples of  $[\text{VO}(\text{X}_4\text{salen})]$  were measured on a SQUID magnetometer (Fig. 3).

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