

Synthesis and Magnetic Properties of VOB(fsa)₂en·3H₂O with B = Mn and Zn and H₄(fsa)₂en = N,N'-bis(2-hydroxy, 3-carboxybenzylidene)-1,2-Diaminoethane

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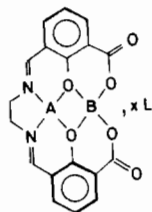
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The bichelating ligand (fsa)₂en⁴⁻ derived from the Schiff base N,N'-bis(2-hydroxy, 3-carboxybenzylidene)-1,2 diaminoethane and used for the first time by Okawa *et al.* [1] has already allowed to obtain a large number of heterobinuclear complexes of formula AB(fsa)₂en·xL (hereafter symbolized by [A B]) [2–6].



A and B are two divalent transition ions occupying the –N₂O₂ and the –O₂O₂ sites respectively and L is a molecule of solvent eventually coordinated or semi-coordinated to one of the transition ions. The magnetic properties of several of these complexes were studied in detail and the parameters characterizing the exchange interaction between the two transition ions were determined [4, 6]. In this latter, we describe the synthesis of two new heterobinuclear complexes of the same family [VO Mn] and [VO Zn] and report their magnetic behaviour. Finally, we compare the results of the magnetic study to those obtained with other [A B] heterobinuclear complexes prepared from the same ligand. This discussion will be focused on the complex [VO Mn] in which the two metallic centres are paramagnetic.

Experimental

The action of VOSO₄·5H₂O in aqueous solution on H₄(fsa)₂en in presence of Na₂CO₃ leads to the mononuclear complex VOH₂(fsa)₂en·2H₂O which precipitates. The lithium salt of this complex is pre-

pared by stirring together 10⁻³ mol of VOH₂(fsa)₂en·2H₂O and 2 × 10⁻³ mol of LiOH·H₂O in 50 cm³ of methanol. Onto this solution a solution of 10⁻³ mol of MnCl₂·4H₂O is added dropwise and VOMn(fsa)₂en·3H₂O precipitates. By using ZnCl₂ instead of MnCl₂·4H₂O, we obtain VOZn(fsa)₂en·3H₂O. *Anal.* VOH₂(fsa)₂en·2H₂O. Found: C, 47.28; H, 4.02; N, 5.92. Calcd: C, 47.26; H, 3.97; N, 6.13. VOMn(fsa)₂en·3H₂O. Found: C, 41.14; H, 3.41; N, 5.29; Mn, 10.47. Calcd: C, 40.93; H, 3.43; N, 5.30; Mn, 10.40. VOZn(fsa)₂en·3H₂O. Found: C, 39.54; H, 3.29; N, 5.29. Calcd: C, 40.14; H, 3.37; N, 5.20.

The infrared spectra of the three compounds exhibit an intense band at 983, 990 and 990 cm⁻¹ respectively, characteristic of the V–O stretching vibration of the vanadyl group.

The magnetic measurements are carried out in the temperature range 3–300 K with a previously described Faraday type magnetometer [4]. The correction of diamagnetism is estimated at –238 × 10⁻⁶ cm³ mol⁻¹. This value is the magnetic susceptibility of the diamagnetic complex [Ni Cd].

Results and Discussion

The molar magnetic susceptibility χ_M for [VO Zn], where only the VO(II) ion is paramagnetic, follows the law

$$\chi_M / \text{cm}^3 \text{ mol}^{-1} = \frac{0.385}{T + 1.4} + 250 \times 10^{-6}$$

In Figure 1 is plotted the temperature dependence of the reciprocal molar magnetic susceptibility χ_M⁻¹ for [VO Mn]. In the range 10–300 K, the magnetic behaviour perfectly obeys the Curie–Weiss law χ_M/

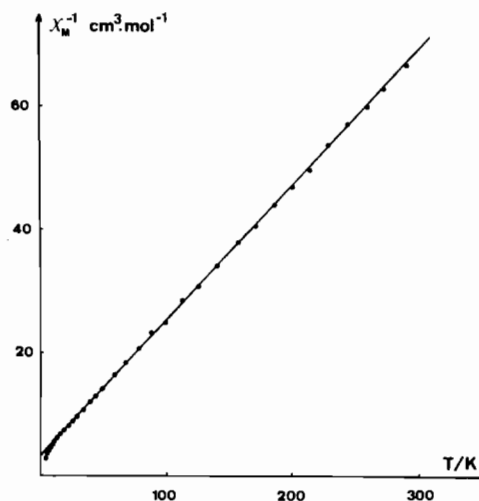


Figure. Variation of χ_M⁻¹ versus T for [VO Mn]

$\text{cm}^3 \text{ mole}^{-1} = 4.59*/T + 13.7$. Below 10K, a very small deviation from this law is observed. This behaviour is very close to that observed for the complex [Zn Mn] in which, in the whole temperature range, only the molecular spin level $S = 5/2$ is populated [4]. This means that the two molecular spin levels $S = 3$ and $S = 2$ arising from the intramolecular exchange interaction in [VO Mn] either are accidentally degenerate, or are largely separated in energy so that only one of them would be populated. The value of the Curie constant shows that the former hypothesis is the good one; the g factor is then 1.966. Therefore the intramolecular exchange interaction parameter J which occurs in the HDVV Hamiltonian $-J \hat{S}_{\text{VO}} \cdot \hat{S}_{\text{Mn}}$ is very close to zero. Considering the accuracy of the magnetic measurements, it can be asserted that $|J|$ is inferior to 5 cm^{-1} . This result can be compared to the one obtained with the complex [Cu Mn] in which, as in [VO Mn], there is one unpaired electron around the magnetic centre occupying the $-\text{N}_2\text{O}_2$ site [4]. For both complexes, the antiferromagnetic intermolecular coupling, characterized by the Weiss constant θ , is important ($\theta = 11.5 \text{ K}$ in [Cu Mn]). This could be due to the oligomeric structure of the [A Mn] complexes (A = Cu, VO or Zn) with bridging oxygen atoms belonging either to water molecules or to $(\text{fsa})_2\text{en}^{4-}$ ligands between Mn(II) ions. On the other hand, the intramolecular couplings are different

($J = -62 \text{ cm}^{-1}$ in [Cu Mn]). Two alternative explanations for this result can be proposed: (i) The site symmetry for both transition ions is C_{2v} . The magnetic orbital centred on the vanadium atom has the a_1 symmetry; it is built from the d_{xy} metallic orbital. Its delocalization on the bridging oxygen atoms involves a $(d_{\pi} | p_{\pi})$ overlap. This may be significantly weaker than the $(d_{\sigma} | p_{\sigma})$ overlap which leads to the delocalization on the bridging oxygen atoms of the b_1 magnetic orbital centred on the Cu(II) ion in [Cu Mn]. Such a weak probability of finding the unpaired electron of the VO(II) ion on the bridging ligands would lessen both the antiferromagnetic and ferromagnetic contributions to the exchange interaction. (ii) The ferromagnetic contribution between the a_1 magnetic orbital centred on VO(II) and the five magnetic orbitals centred on Mn(II) may be important and compensates the antiferromagnetic one. Such a relatively strong ferromagnetic contribution was found in $\text{CuVO}(\text{fsa})_2\text{en} \cdot \text{CH}_3\text{OH}$ [6].

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*If the magnetic data are corrected for the T.I.P. due to the VO(II) ion and determined in [VO Zn], i.e. $250 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, the law becomes $\chi_{\text{M}}/\text{cm}^3 \text{ mol}^{-1} = 4.52/T + 13.0$.