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Magnetic Properties of a Polymeric N,N'-Ethylenebis(salicylideneiminato)oxovanadium(IV) Derivative

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Low-dimensional magnetic materials are actively investigated and many new different types of structural arrangements have been described, including simple linear chain, alternating linear chain, ladder systems, ordered bimetallic linear chain, *etc.* [1–4].

Recently Floriani *et al.* reported the crystal structure of $[(\mathrm{VOSALen})_2\mathrm{Na}]\mathrm{BPh}_4$, where SALen = N,N'-ethylenebis(salicylideneiminato) and BPh_4 = tetraphenylborate, in which a central sodium ion is bridged to four different oxovanadium(IV) ions by six oxygen atoms in a distorted octahedral coordination [5]. Two of the VOSALen molecules bind to the sodium ion through the two oxygen atoms of the SALen moiety, while the remaining two VOSALen molecules bind through the oxovanadium group. The scheme of the coordination around the sodium ion is shown in Fig. 1. In Fig. 1a the connection of the coordination polyhedra is shown, while in Fig. 1b only the metal atoms are shown, with the indication of the possible different exchange interactions.

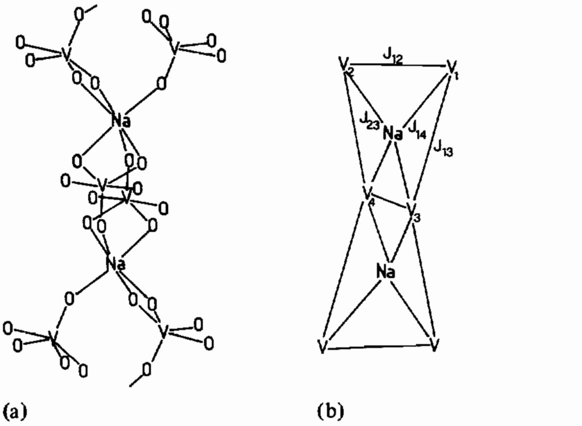

Fig. 1. Schematic representation of the coordination around the sodium ion (a) and of the possible exchange interactions among the vanadyl ions (b).

The sodium ions define a chain, while the vanadium ions define a ribbon made from two twisted zig-zag chains. The ribbons are well separated from each other by the BPh_4^- ions.

It appeared of interest to us to investigate whether the bridging sodium ions could offer a convenient pathway for transmitting the exchange interaction between the VOSALen molecules. We also wished to relate the magnetic structure to the crystal structure, determining the relation between structural and spin dimensionality.

Results and Discussion

The magnetic moments of $[(\mathrm{VOSALen})_2\mathrm{Na}]\cdot\mathrm{BPh}_4$ at room temperature and at 4.2 K are practically the same so that a detailed temperature dependence of the magnetic susceptibility of the compound was measured only in the range 1.2–4.2 K. The results are shown in Fig. 2 in the form of a χ^{-1} *vs.* T plot. The least squares fit to a Curie-Weiss behavior yielded $C = 0.373$ and $\theta = -0.059$, showing that the interaction among the oxovanadium(IV) ions is indeed very small, confirming that the sodium ions are ineffective in transmitting the exchange interaction between the vanadium ions. Similar results were previously obtained from the analysis of the EPR spectra of organic radicals bound to alkali metal ions, which showed that the zero field splitting of the triplet was entirely due to dipolar

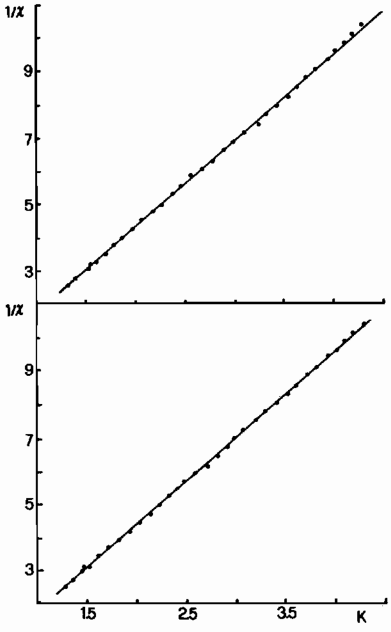

Fig. 2. χ^{-1} *vs.* T plot of experimental data (●). Solid lines are the curves calculated with the best fit parameters using a linear chain model (top) and a Bleaney-Bowers model (bottom) (see text).

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effects, no evidence being found of the exchange interaction between the two radicals [6].

Looking at the structure in Fig. 1b, and assuming ing that the magnetic orbitals are *xy* in nature and orthogonal to the V=O bond, the main possibility of interaction is between pairs of oxovanadium ions bridged by the sodium ion through equatorial oxygen atoms. In this hypothesis the magnetic chain reduces to a chain of non interacting pairs, therefore we attempted a fit using the Bleaney-Bowers equation for $S = ½$ interacting ions. The best fit parameters are $g = 2.123(1)$, $J = 0.15(1)$ cm^{-1}, with an hamiltonian defined as $H = JS_1 \times S_2$, with a discrepancy factor, r defined as $(\Sigma_i(\chi_i^{obs} - \chi_i^{calc})^2/\Sigma_i(\chi_i^{obs})^2)^{1/2}$ equal to 1.70×10^{-3}.

Confirmation of this interpretation comes from the EPR spectra which show a weak feature at half field, indicative of the $\Delta M = 2$ transition within a triplet.

Obviously there are several other possibilities, as shown by the scheme in Fig. 1b. For instance, if only the J_{14} coupling constants were considered on the justification that this could be a 180° pathway while all the others are 90° pathways, the magnetic structure would be that of a linear chain. Using the Bonner-Fisher approach for a linear chain of antiferromagnetically coupled $S = ½$ species [7], we found as best fitting parameters $g = 2.017(1)$ and $J = 0.046(2)$ cm^{-1}, without a significant improvement of the r factor. We did not proceed further however, since the extent of the magnetic interaction is much smaller than our lowest temperature, thus making any detailed interpretation of the data impossible.

Experimental

The compound was prepared according to a reported procedure [5] and was satisfactorily analyzed for C, H and N.

The EPR spectra were recorded with a Bruker ER200 spectrometer. The magnetic susceptibilities were measured by an ac mutual inductance technique at near zero field [8].

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