Ferromagnetic coupling by diamagnetic metal cation coordination: magnetism and structure of the alkali-metal salts of nitroxide carboxylates

Andrzej Misiolek,[a] Rui Huang,[a] Bart Kahr[b] and James E. Jackson*[a]

[a] *Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824-1322, USA*

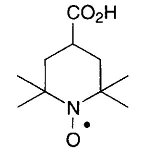
[b] *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA*

Sodium and potassium salts of the free radical 4-carboxy-TEMPO (1-H) form extended one-dimensional ferromagnetically coupled systems: the salt (1-Na) is structurally characterized.

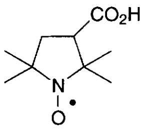
Complexation between diamagnetic metal ions and stable paramagnetic organic species can meet two of the crucial conditions for the preparation of molecular ferromagnetic materials: establishment of high spin coupling between basic building blocks, and their assembly into three-dimensional extended structures. We have reported previously the structural analysis and preparation of several related triaryl compounds and their complexes with alkali-metal salts.[1] This approach did not yield the hoped-for high-spin coupling; apparently the interactions of the cations with neutral radicals were too weak. Examples of high-spin interactions, however, are well known between anionic radicals in the coordination sphere of diamagnetic cations.[2] Placing negative charge on a paramagnetic molecule should strengthen interactions by shortening distances and removing diamagnetic counter anions that would compete for space in the coordination sphere. To verify this hypothesis we have investigated the magnetic properties of the lithium, sodium and potassium salts of two commercially available[†] nitroxyl free-radical carboxylic acids: 4-carboxy-TEMPO (**1-H**) and 3-carboxy-PROXYL (**2-H**).

All the species investigated are paramagnetic, but **1-Na** and **1-K** show weak ferromagnetic coupling as indicated by positive Weiss constants (Table 1).

Ferromagnetic coupling was confirmed by temperature- and field-dependent magnetization measurements. In order to examine magneto-structural correlations in more detail, data were fitted both to the Bleaney–Bowers equation[3] for isotropic spin exchange in dimers of $S = 1/2$ subunits and to the equation of Baker *et al.*[4] for noninteracting isotropic linear ferromagnetic chains. Measurements and fitting repeated on different preparations showed that the latter equation better describes the magnetic behaviour of both compounds (Fig. 1). The values of $2J/k$ were 0.35 K for **1-Na** and 0.37 K for **1-K**. The Bleaney–Bowers equation did not fit so well and could not explain correctly the magnetic behaviour of the samples at low temperatures where χT exceeded the 0.5 maximal value possible for independent high-spin dimers.



1-H
4-carboxy-TEMPO



2-H
3-carboxy-PROXYL

Table 1 Weiss constant values of investigated compounds fitted in the temperature range 2–200 K

Compound	θ/K
1-H	*ca.* −20
1-Li	−1.4
1-Na	+0.5
1-K	+0.6
2-H	*ca.* −10
2-Li	−2.1
2-Na	−0.5
2-K	−1.9

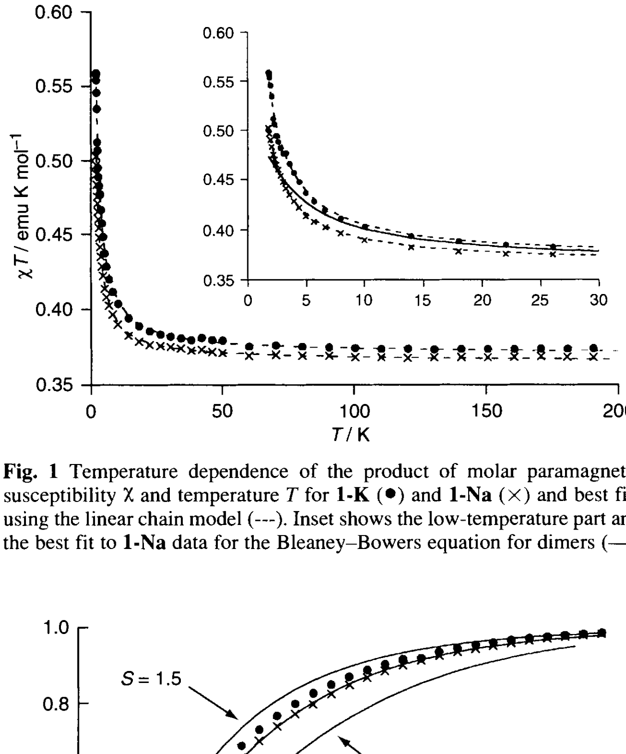


Fig. 1 Temperature dependence of the product of molar paramagnetic susceptibility χ and temperature T for **1-K** (●) and **1-Na** (×) and best fits using the linear chain model (---). Inset shows the low-temperature part and the best fit to **1-Na** data for the Bleaney–Bowers equation for dimers (—).

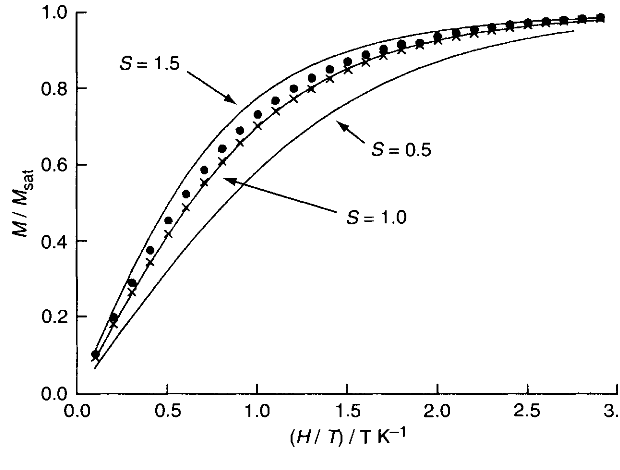


Fig. 2 Magnetic saturation of **1-K** (●) and **1-Na** (×) at 1.9 K. The solid lines (—) are calculated using the Brillouin equation for S = 0.5, 1 and 2.

In order to better assess this interpretation, magnetic saturation studies were carried out (Fig. 2). The Brillouin equation applied to the data with spin multiplicity as a parameter yields $S = 1.01$ at 1.9 K for **1-Na** and 1.20 for **1-K**. At 2 K, values of S were 0.99 and 1.16, respectively.

We were able to grow a single crystal of **1-Na** (yellow thin needle) suitable for X-ray analysis‡ by slow evaporation of an ethanol–acetonitrile solution at room temperature. The salt crystallized in the $P2_1/n$ space group with one crystallographically independent molecule and no atoms at special positions. Each sodium cation is complexed by one nitroxyl and three carboxylate oxygens, at distances of 2.34, 2.31, 2.27 and 2.27 Å, forming a distorted tetrahedral coordination sphere. The sodium cations form zigzag chains parallel to each other and perpendicular to the plane of Fig. 3. In accordance with the magnetic data interpretation, these chains are separated from each other by hydrophobic magnetically insulating segments.

Within the chains (Fig. 4), the sodium cations are bridged by carboxylate groups that position them at alternating 3.37 and 3.79 Å distances from each other. Each coordination centre is related to its neighbours by inversion centres. The shortest communication between unpaired spins appears to lead through the Na_2O_2 parallelograms, while the longer connection leads along two carboxylate anions (solid lines in Fig. 4).

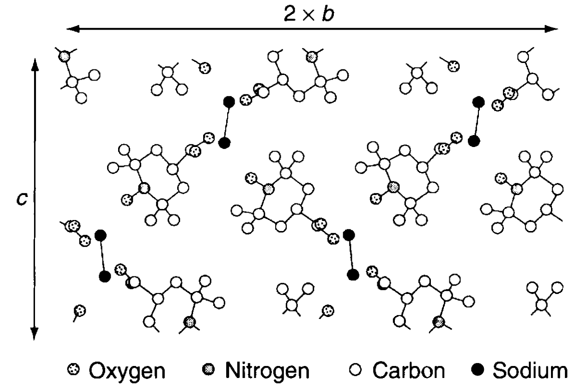


Fig. 3 View along the a axis of **1-Na** showing sodium zigzag chains perpendicular to the plane of view

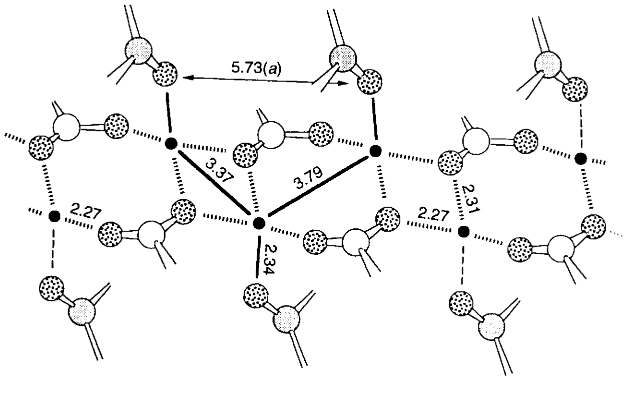


Fig. 4 Side view with dimensions (in Å) of sodium chains, showing coordination of sodium cations by carboxylate and nitroxyl groups. The a dimension (5.73 Å) is also shown.

In both cases, down to the lowest attainable temperature (1.8 K) the χT plot showed no downturn indicating that ferromagnetic ordering of these salts might be possible at a very low temperature due to dipolar interactions.

Although ferromagnetic coupling in a lithium salt of a nitroxide, *p*-(1-oxyl-3-oxido-4,4,5,5-tetramethyl-2-imidazolin-2-yl)benzoic acid, has been reported previously,[5] the lithium cations appeared in that case to be passive in the ferromagnetic coupling transmission. In the present case the sodium cations appear to play an important role in the coupling pathways, though the intended geminal contact of paramagnetic centres in the coordination spheres of alkali- metal cations was not achieved. This is a new example of a molecular material in which diamagnetic cations mediate extended ferromagnetic interactions. The fact that the ferromagnetic behaviour is similar for the two salts of **1-H** encourages us to search for more general phenomena which can be employed in the rational design of molecular magnetic materials. Further investigations will probe the nature of these interactions and the role played by the metal cations.

Footnotes

† Aldrich Chemical Company, Inc.

‡ *Crystal data*: $C_{10}H_{17}NNaO_3$, $M = 222.23$, monoclinic, space group $P2_1/n$, $a = 5.7335(51)$, $b = 13.2058(116)$, $c = 14.2534(80)$ Å, $\beta = 93.722(58)°$, $T = 200$ K, $U = 1076.93(1.37)$ Å^3, $Z = 4$, $D_c = 1.370$ g cm^{-3}, $F(000) = 476$, 2213 measured reflections (up to 2θ 50°), collected on a Siemens P-3, four-circle diffractometer with monochromated Mo-Kα radiation (0.71069 Å). No. of parameters 204 for 1511 reflections with $F_o > 3\sigma(F_o)$. Solution SHELX86, refinement TEXSAN, Na, N, O, C anisotropic, H isotropic. $R = 0.035$, $R_w = 0.023$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/215.

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