Inorganica Chimica Acta, 172 (1990) 137–139

Inorganica Chimica Acta
LETTER

Ground $S = 4$ State in a Manganese(II)–Nitronyl Nitroxide Ferrimagnetic Ring

CRISTIANO BENELLI, ANDREA CANESCHI,
DANTE GATTESCHI*, MARIA CHIARA MELANDRI

Department of Chemistry, University of Florence,
via Maragliano 77, Florence (Italy)

and PAUL REY*

Departement de Recherche Fondamentale, CENG, 85X
Grenoble Cédex (France)

(Received February 15, 1990)

Nitronyl nitroxides (NITR), 2-*R*-4,4,5,5-tetramethyl-Δ^2-imidazolyl-1-oxyl-3-oxides, form a large variety of different spin clusters when coordinated to metal ions [1], and unusual spin states can be stabilized as ground states of molecular units in this way. For instance, we reported [2] a ground $S = 12$ state for a hexanuclear complex of formula $[Mn(hfac)_2(NITPh)]_6$, where hfac is hexafluoroacetylacetonate, and a ground $S = 9/2$ state for $Gd(hfac)_3(NITPh)_2$ [3].

Of particular interest are the closed rings of spins, because they can be used to test the models the extrapolation of which provides the thermodynamic properties of infinite chains. Among these, beyond $[Mn(hfac)_2(NITPh)]_6$ mentioned above, we reported [4] also two complexes of formula $[M(hfac)_2(NITEt)]_2$, where M = Ni or Co, in which the nitronyl nitroxide binds in a μ-1,1 fashion to two metal ions, as shown in Scheme 1. The coupling between metal and radical is antiferromagnetic, therefore these compounds provide examples of simple ferrimagnetic rings.

We have now found that $[Mn(F_3bzac)_2(NITMe)]_2$, F_3bzac = benzoyl trifluoroacetonate, has a similar structure, and we want to report it here together with the magnetic properties which show that this compound has a ground $S = 4$ state.

Experimental

Preparation of $[Mn(F_3bzac)_2NITMe]_2$

$Mn(F_3bzac)_2 \cdot 2H_2O$ was prepared by mixing a stoichiometric amount of benzoyl trifluoroacetonate with $Mn(CH_3COO)_2 \cdot 4H_2O$ in water. The radical was prepared as previously described [5, 6]. $Mn(F_3bzac)_2 \cdot 2H_2O$ (0.5 mmol) was dissolved in 100 ml of boiling n-heptane. The solution was mixed, under stirring, with 0.55 mmol of NITMe radical. After a few minutes the violet solution was filtered and allowed to cool down very slowly. Purple crystals were collected after 24 h and analyzed well for $Mn(F_3bzac)_2NITMe$.

Magnetic Measurements

Variable temperature magnetic susceptibility was measured by using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF1200S continuous-flow cryostat and a Bruker B-E15 electromagnet operating at 1.35 T. Diamagnetic corrections were estimated from Pascal's constants.

X-ray Crystallographic Analysis

Diffraction data for $[Mn(F_3bzac)_2NITMe]_2$ were collected at room temperature with an Enraf Nonius CAD4 four-circle diffractometer equipped with Mo Kα radiation. The data were corrected for Lorentz and polarization effects but not for absorption and extinction. Crystal data: $M = 656.46$; monoclinic space group $C2/c$; $a = 27.829(4)$, $b = 11.505(2)$, $c = 24.150(4)$ Å; $\beta = 128.90(5)°$; $Z = 8$; $\rho = 1.449$ g cm^{-3}; $\lambda = 0.71069$ Å. The Patterson map revealed the position of manganese atoms while the other atoms were found by successive Fourier synthesis using the SHELX-76 package [7]. Anisotropic thermal factors were introduced for the heavy atoms, the oxygen, the fluorine, the carbon atoms of the methyl groups, and those of the phenyl groups bound to the hydrogen atom. Hydrogen atoms were introduced in fixed and idealized positions with isotropic thermal parameters 20% larger than those of the relative carbon atoms. The refinement with 2879 $|F_o| \geqslant 4\sigma|F_o|$ converged to final values of $R = 0.069$ and $R_w = 0.081$.

Results and Discussion

The crystal structure of $[Mn(F_3bzac)_2(NITMe)]_2$ consists of centrosymmetric dimers, as shown in Fig. 1. Each manganese(II) ion is hexa-coordinated by two F_3bzac molecules and two oxygen atoms of two different NITMe radicals, so that the nitroxyl group acts as a μ-1,1 bridging ligand. The metal–F_3bzac oxygen distances are fairly similar to each

---

*Authors to whom correspondence should be addressed.

0020-1693/90/$3.50

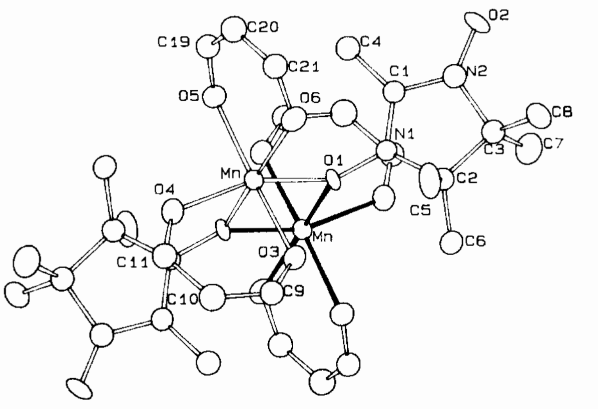

Fig. 1. ORTEP view of the $[Mn(F_3bzac)_2(NITMe)]_2$ molecule.

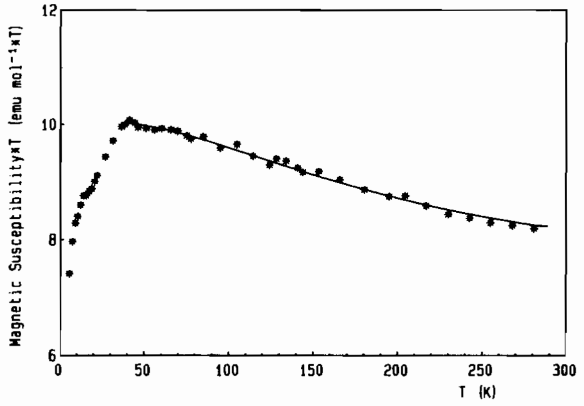

Fig. 2. χT vs. T product for $[Mn(F_3bzac)_2NITMe]_2$. The solid line represents the best fit (see text).

other, ranging from 2.114(4) to 2.157(6) Å, while the manganese–NITMe oxygen distances are longer, 2.224(4) and 2.281(5) Å. The manganese–manganese distance is 3.646(2) Å, and the Mn–O_1–Mn angle is 108.1(2)°. The other O–Mn–O angles are closer to 90°, as expected. The nitronyl nitroxide fragment has its usual shape. The N_1–O_1 distance, 1.320(3) Å, is longer than the N_2–O_2 distance, 1.272(4) Å. No relevant interdimer contacts are observed.

The temperature dependence of χT for $[Mn(F_3bzac)_2(NITMe)]_2$ is shown in Fig. 2. The room temperature value corresponds to $\mu_{eff} = 7.8\ \mu_B$. On cooling χT increases until below 100 K it reaches a plateau corresponding to $\mu_{eff} = 8.9\ \mu_B$, which agrees well with that expected for $S = 4$. The nature of the ground state is confirmed by polycrystalline powder EPR spectra recorded at 4.2 K which show a fine structure of *c.* 1000 G with four transitions at fields higher than H_0. As is often the case for these large spin systems, the low-field transitions are complicated by the presence of forbidden transitions.

The temperature dependence of χT and the low temperature limit both agree with a ferrimagnetic ring of alternating $S = 5/2$ and $S = 1/2$ spins. If we assume that the manganese–radical interactions are identical, the energy levels can be expressed as [8]

$$E(S_{12}S_{34}S) =$$

$$\tfrac{1}{2}J_{12}[S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)]$$

$$+\tfrac{1}{2}J_{34}[S_{34}(S_{34}+1) - S_3(S_3+1) - S_4(S_4+1)]$$

$$+\tfrac{1}{2}J[S(S+1) - S_{12}(S_{12}+1) - S_{34}(S_{34}+1)]$$

where subscripts 1 and 2 refer to manganese, and 3 and 4 to the radical; $S_{12} = S_1 + S_2$, $S_{34} = S_3 + S_4$, $S = S_{12} + S_{34}$.

If only nearest-neighbor interactions are included, i.e. if only J is allowed to be different from zero and positive, the magnetic behavior is that expected [9] for ferrimagnetic rings, with χT initially decreasing, passing through a minimum at $T_{min} = 2.45$ J/k which corresponds to $\mu_{eff} \simeq 7.9\ \mu_B$, and then increases reaching a plateau corresponding to $S = 4$, $\mu_{eff} = 8.9\ \mu_B$. The fact that we see χT increasing on decreasing temperature means that the minimum is at higher temperatures than 300 K.

If we fit quantitatively the data we find $J = 142$ cm^{-1}, a value much smaller than that previously reported for μ-1,3 bridging nitronyl nitroxides with manganese [10]. A similar decrease in the coupling constant was previously observed for nickel(II) [11] for which $J > 400$ cm^{-1} for μ-1,3 coordination and *c.* 100 cm^{-1} for μ-1,1 coordination [3]. The decrease in the coupling is easily understood on the basis of overlap considerations: apparently the overlap between the metal and radical magnetic orbitals decreases when the metal binds in a μ-1,1 fashion compared to the μ-1,3 fashion.

Supplementary Material

Detailed reports for structure determinations including tables for fractional coordinates of non-hydrogen atoms, interatomic distances and intramolecular angles, anisotropic thermal parameters, hydrogen parameters and structure factors (24 pages) are available from the authors on request.

Acknowledgements

The financial support of CNR, Progetto Finalizzato ‘Materiali Speciali per Tecnologie Avanzate’ and MURST is gratefully acknowledged.

References

1 A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Acc. Chem. Res., 22* (1989) 392.

2 A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli and C. Zanchini, *J. Am. Chem. Soc., 110* (1988) 2795.

3 C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier and P. Rey, *Angew. Chem., Int. Ed. Engl., 26* (1987) 913.

4 A. Caneschi, D. Gatteschi, J. Laugier, P. Rey and R. Sessoli, *Inorg. Chem., 27* (1988) 1553.

5 M. Lamchem and T. W. Wittag, *J. Chem. Soc. C,* (1966) 2300.

6 E. F. Ullman, L. Call and J. H. Osiecky, *J. Org. Chem., 35* (1970) 3623.

7 G. Sheldrick, *SHELX 76,* system of computing programs, University of Cambridge, U.K., 1976; C. K. Johnson, *ORTEP, Rep. ORNL 3794,* Oak Ridge National Laboratory, TN, 1965.

8 A. Bencini and D. Gatteschi, in *EPR of Exchanged Coupled Systems,* Springer, Berlin, 1990.

9 M. Verdaguer, *Ph.D. Thesis,* Université de Paris Sud, Orsay, France, 1984.

10 A. Caneschi, D. Gatteschi, P. Rey and R. Sessoli, *Inorg. Chem., 27* (1988) 1756.

11 A. Caneschi, D. Gatteschi, J.-P. Renard, P. Rey and R. Sessoli, *Inorg. Chem., 28* (1989) 2940.