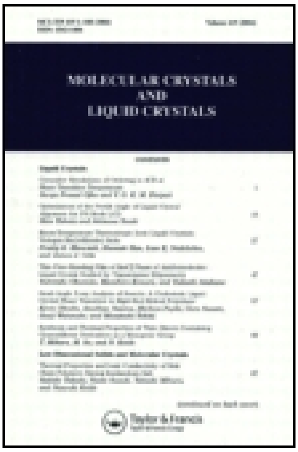
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 11:16
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Manganese(II) Complexes of Nitronyl Nitroxide Radicals. Synthesis, Structure and Magnetic Properties

Dominique Luneau [a] & Paul Rey [a]

[a] Laboratoire de Chimie de Coordination (URA CNRS 1194), CEA-DRFMC-SESAM, Centre d'Etudes Nuclcaires, 17 rue des Martyrs, 38054, Grenoble Cedex 9, France

Version of record first published: 24 Sep 2006.

To cite this article: Dominique Luneau & Paul Rey (1995): New Manganese(II) Complexes of Nitronyl Nitroxide Radicals. Synthesis, Structure and Magnetic Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 273:1, 81-87

To link to this article: http://dx.doi.org/10.1080/10587259508031844

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1995, Vol. 273, pp. 81–87
Reprints available directly from the publisher
Photocopying permitted by license only

© 1995 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

NEW MANGANESE(II) COMPLEXES OF NITRONYL NITROXIDE RADICALS. SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES

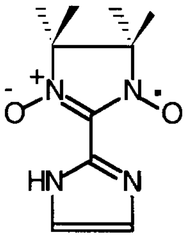
DOMINIQUE LUNEAU AND PAUL REY
Laboratoire de Chimie de Coordination (URA CNRS 1194), CEA-DRFMC-SESAM,
Centre d'Etudes Nucléaires, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.

Abstract The complex $Mn(NITImH)_3(ClO_4)_2$ [NITImH=2-(2-imidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy)] has been synthesized. It crystallizes in the monoclinic space group $P2_1/n$, with a=15.832(3)Å, b=10.346(3)Å, c=26.029(4)Å, β=106.78(1)°and Z=4. The crystal structure consists of $[Mn(NITImH)_3]^{2+}$ cations and non-coordinated perchlorate anions. Each NITImH nitronyl nitroxide radical is bis-chelated to the manganese(II) ion through an oxygen atom of one of its NO groups and a nitrogen atom of the imidazolyl substituent. The coordination geometry around the manganese(II) ion is slightly distorted from octahedral. The perchlorate anions weakly hydrogen bond the $[Mn(NITImH)_3]^{2+}$ cations in a tridimensional network. Cryomagnetic investigations in the range 2-300K revealed a strong antiferromagnetic behavior. The χT product is $2.91 cm^3.K.mol^{-1}$ at 300K, reaches a plateau ($1.00 cm^3.K.mol^{-1}$) between 65 and 15K, then decreases abruptly. The experimental magnetic data were fit assuming identical nitroxide-manganese(II) coupling $J=-53cm^{-1}$ based on the isotropic model $H=-2\Sigma J_{ij}S_iS_j$ associated with an intermolecular antiferromagnetic interaction $Z'J'=-1.4cm^{-1}$ based on the molecular field approximation and g=2.06.

INTRODUCTION

The design of molecular ferromagnets based on the coordination chemistry of nitronyl nitroxide radicals, 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazoyl-1-oxy-3-oxide (NITR), is promising. One way to achieve this is to synthesize extended compounds in which antiferromagnetically coupled metal and radical spin carriers alternate and do not compensate, leading to ferrimagnetic materials. This was succesfully demonstrated by the synthesis and characterization of one-dimensional magnetic materials, using hexafluoroacetylacetonatomanganese(II) and nitronyl nitroxide radicals with alkyl substituents[1]. However the low temperatures (8K) at which these materials order ferromagnetically may be accounted for by the bulkiness of the hexafluoroacetylacetonato ligands surrounding the metal ion. Such electron-withdrawing[2] groups are required to overcome the weak basicity of the nitroxide radical[3] but they isolate the chains and do not allow strong interchain magnetic interactions.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013



NITImH

In order to avoid these bulky groups we are presently engaged in the synthesis of new nitronyl nitroxide radicals with strong donor substituents which would force the coordination of the NO groups through a chelate effect and there by would increase the dimensionality of the compounds. In previous papers we reported the crystal structure and magnetism of nickel(II), manganese(II) and copper(II) complexes with 2-pyridyl[4] or 2,2'-bipyridyl[5] substituted nitronyl nitroxide showing that chelation was an effective force for coordination of the nitroxyl group to poorly electrophilic metal centers.

Along this line we have synthesized the 2-imidazolyl substituted nitronyl nitroxide (NITImH), for which the position of the 2-imidazolyl group allows two symmetrical chelating sites for the synthesis of extended materials. One of the sites is directly accessible; the second one may be generated after deprotonation to give the bis chelate anion ($NITIm^-$). In a first step, and before any attempt to make extended compounds, we have studied the complexation of the non- deprotonated ligand (NITImH) with various metal ions in order to characterize the nitroxide-metal magnetic interaction in our molecular units. In this paper we describe the synthesis, crystal structure and magnetic properties of the complex $Mn(NITImH)_3(ClO_4)_2$ formed with the manganese(II) perchlorate salt.

EXPERIMENTAL SECTION

Syntheses.

The 2-imidazolecarboxaldehyde was purchased from Aldrich while the 2,3-(dihydroxylamino)-2,3-dimethylbutane was prepared by following reported procedures[6]. The free radical was obtained as described by Ullman[7] for the phenyl substituted analogue (47%, mp=150-152°C).

$Mn(NITImH)_3(ClO_4)_2$. Methanol solutions of both NITImH and $Mn(ClO_4)_2.6H_2O$ in stoechiometric amounts were mixed. The resulting blue solution was then filtrated and allowed to evaporate slowly to a small portion to give dark blue parallelepipedic single crystals (65%). The elementary analysis agree well with the formula $C_{30}H_{45}N_{12}O_8Mn(ClO_4)_2$.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013

X-ray crystal structure analysis.

TABLE I Cystal data, intensity data collections and structure refinement.

Formula	$C_{30}H_{45}N_{12}O_{14}Cl_2Mn$	Scan type	$\omega-\theta$
F.W.	923.6	Scan width (°)	$0.80+0.35tg\theta$
Crystal system	Monoclinic	Scan speed ($°.mm^{-1}$)	5.03
Space group	$P2_1/n$	θmax (°)	25
Z	4	Detector height	4
a (Å)	15.832(3)	Detector width	$1.70+2.00tg\theta$
b (Å)	10.346(3)	Octant measd.	±h,+k,+l
c (Å)	26.029(4)	Nb. of measd. refl.	8149
β (°)	106.78(1)	Nb. of unique refl.	4408
V (Å^3)	4081.9	Nb. of parameter	459
Dc (g.cm^{-3})	1.495	Res. elec. d. (e.Å^{-3})	-0.48, +0.87
μ(MoKα) (cm^{-1})	5.0	Maximum esd	0.004
Cryst. size (mm)	0.35*0.25*0.25	Weigting scheme	$1/\sigma_F^2 + 3.10^{-3}F^2$
Temperature (K)	293	R	0.0532
Diffractometer	Enraf-Nonius	Rw	0.0571

The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using MoKα radiation and a graphite monochromator. Crystal structure data are summarized in TABLE I. Cell constants were derived from a least-squares fit of the setting angles for 25 selected reflections with $10° \leq \theta \leq 15°$ The intensities were corrected for Lorentz and polarization effects but not for absorption. The Mn(II) ion position was found using the SHELX86[8] package. The remaining non-hydrogen atoms were located in a succession of difference Fourier syntheses and were least-squares refined with anisotropic thermal parameters using the SHELX76[9] package. The hydrogen atoms, except those attached to the nitrogen atoms (NH) of the imidazolyl groups, were included in the final refinement model in calculated and fixed positions with isotropic thermal parameters. Morever the agreement between the single crystal structure and the bulk material has been checked by comparing the experimental powder X-ray diffraction patern to the simulated one obtained from the single-crystal data with the LAZY PULVERIX[10] program.

Magnetic Susceptibility Measurements.

The magnetic susceptibility was measured on the bulk material, in the 2-300K temperature range with a Quantum Design MPMS superconducting SQUID magnetometer operating at field strength of 0.5 T. The data were corrected for the magnetization of the sample holder and the magnetic susceptibility was corrected for the diamagnetism of the constituent atoms using Pascal constants.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013

RESULTS AND DISCUSSION

Crystal Structure.

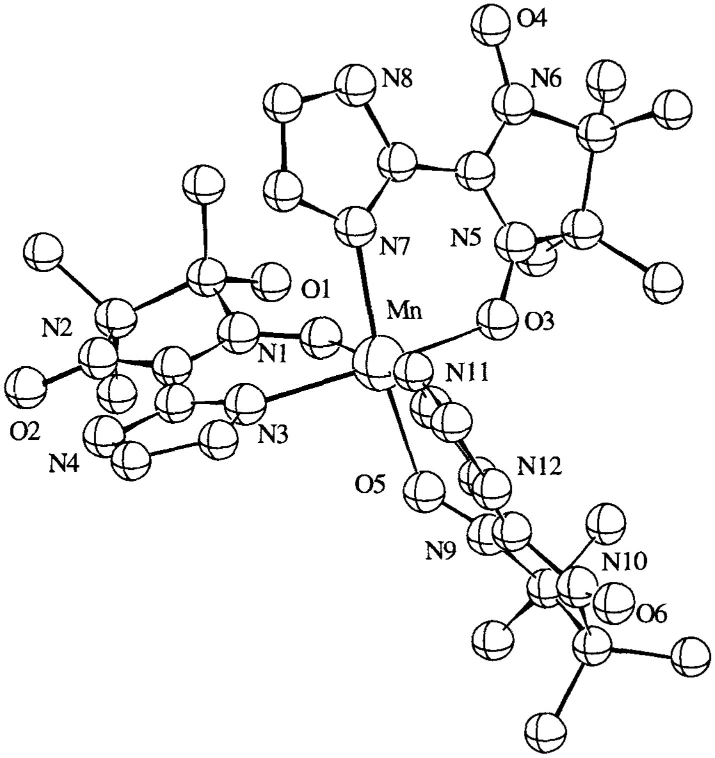


FIGURE 1 View of $[Mn(NITImH)_3]^{2+}$ with labeling of non-carbon atoms.

TABLE II Relevant interatomic distances (Å) and angles (°).

Mn-O1	2.175 (4)	Mn-O3	2.135 (3)
Mn-O5	2.178 (3)	Mn-N3	2.224 (3)
Mn-N7	2.211 (4)	Mn-N11	2.206 (4)
O1-N1	1.287 (4)	O2-N2	1.269 (6)
O3-N5	1.291 (5)	O4-N6	1.270 (6)
O5-N9	1.306 (4)	O6-N10	1.278 (5)
O13-H(N8)i	2.335 (8)	O11-H(N12)ii	2.109 (9)
O1-Mn-N3	83.1 (1)	O1-Mn-O3	86.4 (1)
O1-Mn-N7	85.8 (2)	O1-Mn-O5	92.4 (2)
O1-Mn-N11	172.2 (2)	N3-Mn-O3	169.4 (1)
N3-Mn-N7	93.9 (2)	N3-Mn-O5	96.6 (1)
N3-Mn-N11	91.2 (2)	O3-Mn-N7	84.8 (2)
O3-Mn-O5	84.4 (1)	O3-Mn-N11	99.4 (2)
N7-Mn-O5	169.1 (2)	N7-Mn-N11	100.0 (2)
O5-Mn-N11	82.9 (2)	Mn-O1-N1	129.1 (2)
Mn-O3-N5	128.1 (3)	Mn-O5-N9	125.5 (3)

*:x,y-1,z; ii:x-1/2,y+1/2,z-1/2

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013

The crystal structure consists of the $[Mn(NITImH)_3]^{2+}$ cation shown in FIGURE 1 and of perchlorate anions located out of the Mn(II) coordination sphere. Relevant bond lengths and angles are given in TABLE II. Each of the three NITImH ligands is bis-chelated to the Mn(II) ion through an oxygen atom of one of its NO groups and a nitrogen atom of the imidazolyl substituent. The manganese(II) coordination geometry in $[Mn(II)(NITImH)_3]^{2+}$ is octahedral with both the Δ or Λ isomer forms encountered in the crystal cell due to the centrosymmetric $P2_1/n$ space group. These conformations minimise the steric hindrance by keeping apart the 2,3-dimethylbutyl groups of the three nitronyl nitroxides. The bond angles within the coordination octahedron are significantly distorted while the Mn-O and Mn-N bond lengths are in the normal range 2.135(3)-2.178(4)Å and 2.206(4)-2.211(4)Å respectively for manganese(II)-nitroxide complexes. The shortest intermolecular distances reported in TABLE II have been found between the oxygen atoms O11 and O13 of one of the perchlorate anions and the hydrogen atoms H(N12) and H(N8) of the imidazolyl group of two adjacent $[Mn(II)(NITImH)_3]^{2+}$ cations. They are part of a tridimensional hydrogen bond network connecting the $[Mn(II)(NITImH)_3]^{2+}$ units weakly to each other through the perchlorate anions.

Magnetic properties.

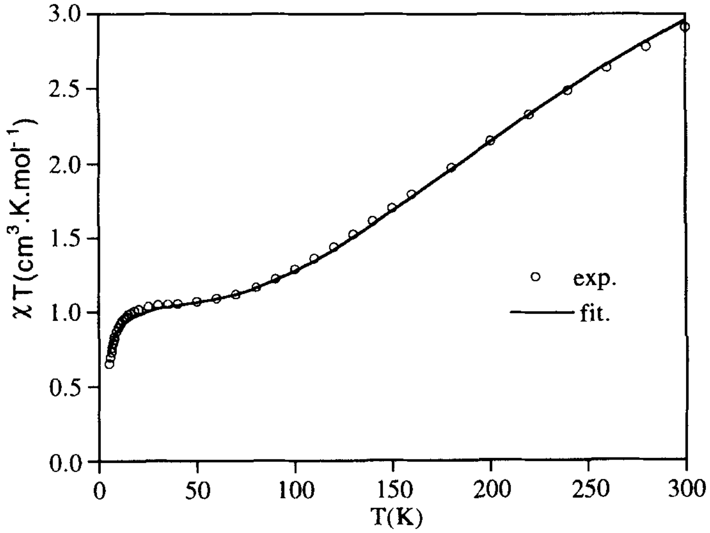


FIGURE 2 Plots of χT *vs*. T (o experimental, -------- fit).

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013

The magnetic behavior shown by $Mn(NITImH)_3(ClO_4)_2$ on FIGURE 2 as the product of the magnetic susceptibility with temperature (χT) *versus* temperature, is characteristic of a strong antiferromagnetic coupling. At 300K $\chi T=2.91 cm^3.K.mol^{-1}$ is well below the value ($5.5\ cm^3.K.mol^{-1}$) expected for one Mn(II) 5/2 spin and three uncoupled NITImH 1/2 spins. Then χT continuously decreases and reaches a plateau between 60 and 15K with a value of χT ($1\ cm^3.K.mol^{-1}$) in agreement with a S=1 ground state corresponding to the Mn(II) 5/2 spin antiferromagnetically coupled with three NITImH 1/2 spins. Below 15K, χT decreases abruptly due to the intermolecular magnetic interactions transmited through the weak intermolecular hydrogen bond network as suggested from the X-ray crystal structure analysis. Although analytical expressions for the magnetic susceptibility might be derived, we used a homemade program[11] coupled to the Minuit minimization routine, which diagonalizes numerically the isotropic exchange Hamiltonian ($H=-2\Sigma J_{ij}S_iS_j$) for a cluster constituted of one 5/2 spin interacting with three 1/2 spins. We considered the three nitroxide-manganese(II) magnetic interactions as identical and took no account of the nitroxide-nitroxide radical interactions. Moreover, in order to fit the sharp decrease at low temperature we included in the model an intermolecular interaction (Z'J') considering the molecular field approximation[12]. A good agreement was obtained for the overall temperature range with an antiferromagnetic nitroxide-manganese(II) interaction $J=-53cm^{-1}$, an intermolecular interaction $Z'J'=-1.4cm^{-1}$ and g=2.06 as shown in FIGURE 2. The nitroxide-manganese(II) interaction found here is lower in magnitude than those reported for previous nitroxide-manganese(II) complexes[4,13], however the comparison with copper(II)-manganese(II) compounds[14] still shows that stronger interactions are obtained between manganese and radicals.

CONCLUSION

The bis-chelating ligand NITImH affords for the first time a complex in which the octahedral coordination sphere of a poorly electrophilic metal center is completed solely by nitronyl-nitroxide radicals showing once again the effectiveness of the chelating effect to force the coordination of the nitroxyl group. Morever a strong manganese(II)-nitroxide antiferromagnetic interaction ($-53cm^{-1}$) is observed. This is of importance or one who wants to synthesize a ferromagnet with the ferrimagnetic approach, for the antiferromagnetic coupling between the uncompensated spins must be as high as possible independently of the required tridimensionality. Indeed the present complex is our molecular unit for building up extended materials and we can reasonably expect the magnitude of the antiferromagnetic nitroxide-manganese(II) interaction to be kept in these compounds. Thus we have recently synthesized both a one- and a two-dimensional compounds for which the structural and magnetic properties studies have not been yet completed but preliminary results show that both compounds exhibit a ferrimagnetic behavior with the minimum of the χT product (or the long range correlation betweens the spins) to be above 200K as expected for an antiferromagnetic nitroxide-manganese(II) interaction in the range of -50cm^{-1} (kT/J=2.98 for a 1/2-5/2 chain)[15].

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:16 18 February 2013

REFERENCES

1] A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli, Inorg. Chem., 28, 3314 (1989).

2] R.A. Zelonka, M.C. Baird, J. Am. Chem. Soc, 93, 6066-6070 (1971)

3] (a) Y.Y. Lim, R.S. Drago, J. Am. Chem. Soc., 93, 891-894 (1971), (b) Y.Y. Lim, R.S. Drago, Inorg. Chem., 11, 1334-1338 (1971). (c) R.M. Richman, T.C. Kuechler, R.S. Drago, J. Am. Chem. Soc., 99, 1055-1058 (1977). (d) R.S. Drago, T.C. Kuechler, M. Kroeger, Inorg. Chem., 18, 2337-2342 (1979)

4] D. Luneau, G. Risoan, P. Rey, A. Grand, A. Caneschi, D. Gatteschi, J. Laugier, Inorg. Chem.,.32, 5616-5622(1993).

5] D. Luneau, J. Laugier, P. Rey, G. Ulrich, R. Ziessel, P. Legoll, M. Drillon, J. Chem. Soc., Chem. Commun., 741-742 (1994).

6] M. Lamchen, T.W. Mittag, J. Chem.Soc. C, 2300, (1966)

7] E.F. Ullman, J.H. Osiecki, D.G.B. Boocock, R. Darcy, J.Am.Chem.Soc., 94, 7049-7059 (1972).

8] G.M. Sheldrick, Crystallographic Computing, Eds. G.M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 175 (1985).

9] G.M. Sheldrick, SHELX76, System of Computing Programs, University of Cambridge, Cambridge, England (1976).

10] K. Yvon, W. Jeitsko, E. Pathe, LAZY PULVERIX program, University of Geneva Switzerland (1977).

11] E. Belorisky, P.H. Fries, E. Gojon, J.M. Latour, Mol. Phys., 61, 661-666 (1987).

12] A.P. Ginsberg, R.L. Martin, R.W. Brookes, R.C. Sherwood, Inorg. Chem., 11, 2884-2889 (1972).

13] (a) M.H. Dickman, C.L. Porter, R.J. Doedens, Inorg. Chem., 25, 2595-2599 (1986). (b) A. Caneschi, D. Gatteschi, J. Laugier, L. Pardi, P. Rey, C. Zanchini, Inorg. Chem, 27, 2027-2032 (1988). (c) A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli, C. Zanchini, J. Am. Chem. Soc., 110, 2795-2799 (1988). (d) M.D. Carducci, R.J. Doedens, Inorg. Chem, 28, 2492-2494 (1989). (e) A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli, Inorg. Chem, 27, 3314-3319 (1989). (f) C. Beneli, A. Caneschi, D. Gatteschi, M.C. Melandri, Inorg. Chim.Acta, 172, 137-139 (1990). (g) A. Caneschi, D. Gatteschi, P. Rey, R. Sessoli, Inorg. Chem., 30, 3936-3941 (1991) (h) E. Belorisky, P. Rey, Mol. Phys., 75, 563-575 (1992).

14] C.Mathonière, O. Kahn, J-C. Daran, H. Hilbig, F.H. Köhlner, Inorg. Chem., 32, 4057-4062 (1993). Y. Pei, Y. Journaux, O. Khan, A. Dei, D. Gatteschi, J. Chem. Soc., Chem. Commun., 1300-1301 (1986). A. Gleize, M. Verdaguer, J. Am. Chem. Soc., 106, 3727-3737 R. Ruiz, F. Lloret, M. Julve, J. Faus, M.C. Munoz, X. Solans, Inorg. Chim. Acta, 213, 261- (1993).

15] M. Verdaguer, A. Gleizes, J-P. Renard, J. Seiden, Phys. Rev., B29, 5144-5155 (1984).