Inorganic Chemistry
Article

Syntheses, Crystal Engineering, and Magnetic Property of a Dicyanamide Bridged Three-Dimensional Manganese(II)–Nitronyl Nitroxide Coordination Polymer Derived from a New Radical[†]

Hsin-Huang Lin,[‡] Sasankasekhar Mohanta,*,[‡,§] Chin-Jhan Lee,[‡,||] and Ho-Hsiang Wei*,[‡]

Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137,
Department of Chemistry, Calcutta University, 92 A. P. C. Ray Road, Kolkata 700 009, India, and
Deh Yu Institute of Technology, Kee Lung, Taiwan 203

Syntheses, structural characterization, crystal engineering, and variable-temperature magnetic study at fixed field strength of a novel dicyanamide bridged three-dimensional manganese(II)–nitronyl nitroxide compound, [Mn^{II}(NIT-tz)(dca)$_2$] (**1**), (NIT-tz = 2-(2-thiazole)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide, a new Ullman type radical) have been described. The compound crystallizes in the orthorhombic $P2_12_12_1$ space group with the following unit cell parameters: a = 11.015(2) Å, b = 12.6134(14) Å, c = 13.7652(9) Å, and Z = 4. In this complex, the radical behaves as a bidentate chelating ligand, while four single end-to-end dicyanamide (dca) units construct the three-dimensional structure. Inside the structure, there exist diamond-shaped channels, spiral networks, and helical chains. Variable-temperature (5–300 K, 1 T) magnetic susceptibility data reveal the existence of antiferromagnetic interaction in this molecule. The magnetic behavior is explained by considering the exchange-coupled manganese(II)–radical system, which is subjected to the Mn^{II}–dca–Mn^{II} intermolecular interactions (H = $-2J\mathbf{S}_1 \cdot \mathbf{S}_2 - 2zJ'\langle \mathbf{S} \rangle S$). The least-squares fitting of the data results J = -73 cm^{-1}, g = 1.99, and J' = -0.17 cm^{-1} (z = 4).

Introduction

Nitronyl nitroxides, independently or in combination with metal ions, have been one of the most widely studied systems in molecular magnetism for understanding the radical–radical or metal–radical interactions as well as for synthesizing organic ferromagnets and metal–radical magnetic materials.[1] In the same frontier field, pseudohalide-bridged coordination compounds have also occupied a dominating position.[2–4] Recently, a more hybrid approach of assembling metal ions, radicals (nitronyl or imino nitroxides), and pseudohalides has been started with the expectation of extracting more fascinating results.[5] So far, azide[5a] or dicyanamide (dca)[5b] coordinated mononuclear, cyanide-bridged clusters with high spin ground state,[5c,d] and dicyanamide or dicyanoargentate(I) bridged 1-D[5b,e,f] and 2-D[5g] compounds have been isolated.

In contrast to azide or cyanide, extensive studies on dca bridged compounds have been started very recently. After the observations of three-dimensional structures and long-range magnetic orderings in binary complexes with 3d metal ions,[4a–c] a vast fascination has been directed to the synthesis

* To whom correspondence should be addressed. E-mail: tkwei@mail.tku.edu.tw (H.-H.W.); s_mohanta@hotmail.com (S.M.). Fax: 886-2-26209924.
[†] Dedicated to the memory of Professor Olivier Kahn.
[‡] Tamkang University.
[§] Calcutta University.
[||] Deh Yu Institute of Technology.

(1) The following publications and references therein are examples of nitronyl nitroxide systems: (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Caneschi, A.; Gatteschi, D. *Prog. Inorg. Chem.* **1991**, *39*, 331. (c) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392. (d) Amabilino, D. B.; Veciana, J. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, 2001; pp 1–60. (e) Iwamura, H.; Inoue, K. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, 2001; pp 61–108. (f) *Magnetic Properties of Organic Molecules*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (g) Rey, P.; Luneau, D. In *Supramolecular Engineering of Synthetic Metallic Materials*; Veciana, J., Rovira, C., Amabilino, D. B., Eds.; NATO ASI Series C Vol. 518; Kluwer Academic Publishers: Dordrecht, 1999; pp 145–174. (h) Fegy, K.; Sanz, N.; Luneau, D.; Belorizky, E.; Rey, P. *Inorg. Chem.* **1998**, *37*, 4518. (i) Luneau, D.; Risoan, G.; Rey, P.; Grand, A.; Caneschi, A.; Gatteschi, D.; Laugier, J. *Inorg. Chem.* **1993**, *32*, 5616. (j) Francese, G.; Romero, F. M.; Neels, A.; Stoeckli-Evans, H.; Decurtins, S. *Inorg. Chem.* **2000**, *39*, 2087. (k) Rancurel, C.; Leznoff, D. B.; Sutter, J.-P.; Golhen, S.; Ouahab, L.; Kliava, J.; Kahn, O. *Inorg. Chem.* **1999**, *38*, 4753. (l) Lee, C.-J.; Huang, C.-H.; Wei, H.-H.; Liu, Y.-H.; Lee, G.-H.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 171.

and studies of dca bridged systems.[4d,e,5b,f,6−12] In addition to the interests in magnetochemistry, due to the presence of three potential donor centers and varieties of possible bridging modes of dca, the dca bridged compounds are also an appealing member in the field of crystal engineering and the design of inorganic coordination polymers which has been a research area of rapidly growing interest due to the potential applications as functional materials as well as for the construction of novel topologies and for the aesthetic beauty.[13] Interesting types of structures such as rutile-like networks[4a−c] and interpenetration[4d,6] have been already observed in dca bridged compounds.

(2) The following publications and references therein are examples of cyanide bridged systems: (a) Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scuiller, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190*, 1023. (b) Ohba, M.; Ōkawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313.

(3) The following publications and references therein are examples of azide bridged systems: (a) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193-195*, 1027. (b) Escuer, A.; Vicente, R.; Mautner, F. A.; Goher, M. A. S.; Abu-Youssef, M. A. M. *J. Chem. Soc., Chem. Commun.* **2002**, 64.

(4) Dicyanamide bridged systems: (a) Manson, J. L.; Kmety, C. R.; Huang, Q.-z.; Lynn, J. W.; Bendele, G. M.; Pagola, S.; Stephens, P. W.; Liable-Sands, L. M.; Rheingold, A. L.; Epstein, A. J.; Miller, J. S. *Chem. Mater.* **1998**, *10*, 2552. (b) Kurmoo, M.; Kepert, C. J. *New J. Chem.* **1998**, *1515*. (c) Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1998**, 439. (d) Manson, J. L.; Kmety, C. R.; Huang, Q.-z.; Lynn, J. W.; Bendele, G. M.; Pagola, S.; Stephens, P. W.; Liable-Sands, L. M.; Rheingold, A. L.; Epstein, A. J.; Miller, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 162. (e) Escuer, A.; Mautner, F. A.; Sanz, N.; Vicente, R. *Inorg. Chem.* **2000**, *39*, 1668.

(5) (a) Fettouhi, M.; Khaled, M.; Uaheed, A.; Golhen, S.; Ouahab, L.; Sutter, J.-P.; Kahn, O. *Inorg. Chem.* **1999**, *38*, 3967. (b) Dasna, I.; Golhen, S.; Ouahab, L.; Daro, N.; Sutter, J.-P. *New J. Chem.* **2001**, *25*, 1572. (c) Vostrikova, K. E.; Luneau, D.; Wernsdorfer, W.; Rey, P.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 718. (d) Marvilliers, A.; Pei, Y.; Boquera, K. E.; Paulsen, C.; Rivière, E.; Audière, J.-P.; Mallah, T. *J. Chem. Soc., Chem. Commun.* **1999**, 1951. (e) Dasna, I.; Golhen, S.; Ouahab, L.; Daro, N.; Sutter, J.-P. *Polyhedron* **2001**, *20*, 1371. (f) Dasna, I.; Golhen, S.; Ouahab, L.; Peña, O.; Guillevic, J.; Fettouhi, M. *J. Chem. Soc. Dalton Trans.* **2000**, 129. (g) Dasna, I.; Golhen, S.; Ouahab, L.; Fettouhi, M.; Peña, O.; Daro, N.; Sutter, J.-P. C. *Inorg. Chim. Acta* **2001**, *326*, 37.

(6) (a) Jensen, P.; Price, D. J.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *Chem.—Eur. J.* **2000**, *6*, 3186. (b) Batten, S. R.; Harris, A. R.; Jensen, P.; Murray, K. S.; Ziebell, A. *J. Chem. Soc., Dalton Trans.* **2000**, 3829. (c) Sun, B.-W.; Gao, S.; Ma, B.-Q.; Wang, Z.-M. *New J. Chem.* **2000**, *24*, 953.

(7) Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1998**, 793.

(8) (a) Vangdal, B.; Carranza, J.; Lloret, F.; Julve, M.; Sletten, J. *J. Chem. Soc., Dalton Trans.* **2002**, 566. (b) Claramunt, A.; Escuer, A.; Mautner, F. A.; Sanz, N.; Vicente, R. *J. Chem. Soc., Dalton Trans.* **2000**, 2627. (c) Marshall, S. R.; Incarvito, C. D.; Manson, J. L.; Rheingold, A. L.; Miller, J. S. *Inorg. Chem.* **2000**, *39*, 1969. (d) Martin, S.; Barandika, M. G.; de Larramendi, J. I. R.; Cortés, R.; Font-Bardia, M.; Lezama, L.; Serna, Z. E.; Solans, S.; Rojo, T. *Inorg. Chem.* **2001**, *40*, 3687. (e) Batten, S. R.; Jenson, P.; Kepert, C. J.; Kurmoo, M.; Moubaraki, B.; Murray, K. S.; Price, D. *J. Chem. Soc., Dalton Trans.* **1999**, 2987.

(9) Triki, S.; Thétiot, F.; Galán-Mascaros, J.-R.; Sala Pala, J.; Dunbar, K. *New J. Chem.* **2001**, *25*, 954.

(10) (a) Manson, J. L.; Lee, D. W.; Rheingold, A. L.; Miller, J. S. *Inorg. Chem.* **1998**, *37*, 5966. (b) Riggio, I.; van Albada, G. A.; Ellis, D. D.; Spek, A. L. *Inorg. Chim. Acta* **2001**, *313*, 120. (c) Manson, J. L.; Schlueter, J. A.; Geiser, U.; Stone, M. B.; Reich, D. H. *Polyhedron* **2001**, *20*, 1423.

(11) (a) Raebiger, J. W.; Manson, J. L.; Sommer, R. D.; Geiser, U.; Rheingold, A. L.; Miller, J. S. *Inorg. Chem.* **2001**, *40*, 2578. (b) van der Werff, P. M.; Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **2001**, *40*, 1718.

(12) Sun, B.-W.; Gao, S.; Ma, B.-Q.; Niu, D.-Z.; Wang, Z.-M. *J. Chem. Soc. Dalton Trans.* **2000**, 4187.

Although in homoleptic[4a−c] and, in a few rare examples of heteroleptic systems,[7] a three-connecting bridging mode has been observed, in most cases, dicyanamide bridges metal ions through the two terminal nitrogens (end-to-end (EE), $\mu_{1,5}$-) which, in the presence of blocking or bridging ligands, can result in zero-,[8a] one-,[4e,5b,f,8] two-,[5g,6b,c,7−11] or three-dimensional structures.[12] Regarding the multidimensional networks formed by only EE dca, the reported results are mostly two-dimensional and are achieved by either of the following bridging ways: three single,[6b,9] four single,[5g,6c,10] or a dual mode of two double and two single.[9,11] Three-dimensional structures constructed by only EE dca are really rare. To the best of our knowledge, there are only two examples of such systems where three-dimensional structures are formed by the linking of four single EE dca.[8d,12]

Although homoleptic M(dca)$_2$ (M = 3d metal ions) systems having the three-connecting bridging mode exhibit long-range ordering, it has been observed experimentally and theoretically that $\mu_{1,5}$-dca, the usual bridging mode in heteroleptic compounds, is a very weak coupler[4e,5−12] of superexchange interactions and, evidently, is not a promising member in molecular magnetism; in a two-dimensional $\mu_{1,5}$- and μ-pyrazine compound of Mn^{II}, antiferromagnetic ordering takes place only at 2.53 K.[4d] However, as described previously, dicyanamide is a genuine bridging ligand for developing coordination polymers. Another blocking or bridging ligand is absolutely necessary for the design of dca bridged heteroleptic supramolecules. Several organic ligands, particularly from pyridine families, have been used for this purpose.[4d,e,5−12] Nitronyl nitroxides have both the blocking and bridging properties[1] and can also be used to fulfill this criteria. If the radical has a chelating nature, it is more expected to behave as a blocking ligand, and in combination with dca, there is the possibility of developing metal−radical units bridged by dicyanamide. In case of a new radical, the derived compounds would serve the dual purposes, namely, enlightenment of the metal−radical magnetic interactions and crystal engineering of the dca networks. With these 2-fold orientations, we report here the syntheses, structural characterization, crystal engineering, and variable-temperature magnetic study of a novel three-dimensional metal ion−nitronyl nitroxide−pseudohalide compound, [Mn^{II}(NIT-tz)-(dca)$_2$], derived from a new nitronyl nitroxide radical (Chart 1, NIT-tz = 2-(2-thiazole)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy-3-oxide). In this compound, the radical acts as bidentate chelating ligand, and the three-dimensional structure is formed by four single EE dicyanamides. Magnetic susceptibility data reveal moderate antiferromagnetic interaction between Mn^{II} and the radical, while weak antiferromagnetic interaction is mediated by dca ligands.

(13) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (c) Blake, J.; Champness, N. R.; Hubberstey, P.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (d) Moulton, B. M.; Zaworotko, J. *Chem. Rev.* **2001**, *101*, 1629. (e) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (f) Braga, D.; Maini, L.; Polito, M.; Scaccianoce, L.; Cojazzi, G.; Grepioni, F. *Coord. Chem. Rev.* **2001**, *216*, 225. (g) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

Chart 1. Chemical Structure of NIT-tz
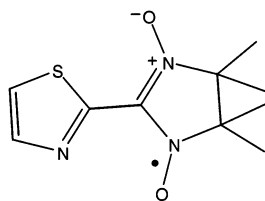
Table 1. Crystallographic Data for [Mn^{II}(NIT-tz)(dca)$_2$] (**1**)

empirical formula	C$_{14}$H$_{14}$N$_9$O$_2$SMn
fw	427.33
space group	$P2_12_12_1$
a, Å	11.015(2)
b, Å	12.6134(14)
c, Å	13.7652(9)
V, Å^3	1912.6(4)
Z	4
T, K	293(2)
λ (Mo Kα), Å	0.71073
μ, cm^{-1}	8.29
ρ_{calcd}, g cm^{-3}	1.484
R1^a ($I > 2\sigma(I)$)	0.0386
wR2^b (all data)	0.0486

^{a} R1 = [$\Sigma||F_o| - |F_c||/\Sigma|F_o|$]. ^{b} wR2 = [$\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2$]$^{1/2}$.
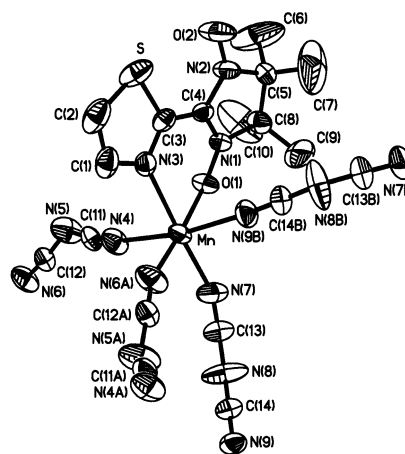
Experimental Section

Materials and Physical Measurements. All the reagents and solvents were purchased from the commercial sources and used as received. 2,3-Bis(hydroxylamino)-2,3-dimethylbutane was prepared by reported method.[14] Elemental (C, H, N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400−4000 cm^{-1} on a Bio-Rad FTS40 spectrophotometer with samples as KBr disks. Variable-temperature (5−300 K) magnetic susceptibility measurements under fixed field strength of 1 T were carried out with a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were estimated from the Pascal's constants.[15]

Syntheses. 2-(2-Thiazole)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy-3-oxide (NIT-tz). This new radical was synthesized by the reported method[16] using 2-thiazolecarboxaldehyde as the starting aldehyde. Yield: 40%. Color: blue. Anal. Calcd for C$_{10}$H$_{14}$N$_3$O$_2$S: C, 49.98; H, 5.87; N, 17.48. Found: C, 49.67; H, 5.96; N, 17.62. IR(KBr): 1373 cm^{-1} (ν_{NO}). EPR (293 K, CH$_2$Cl$_2$): five lines; g = 2.01; a_N = 7.47 G.

[Mn^{II}(NIT-tz)(dca)$_2$] (1). To a stirred solution (5 mL) of Mn-(ClO$_4$)$_2$·6H$_2$O (0.18 g, 0.5 mmol) in methanol was added a blue methanol solution (5 mL) of NIT-tz (0.12 g, 0.5 mmol). After 30 min, 0.1 g (1.12 mmol) of sodium dicyanamide dissolved in 10 mL methanol was added to the resulting solution. The color changed to green. The stirring was continued for a few hours. Then, the mixture was filtered to remove the suspended materials, and the filtrate was kept at room temperature for slow evaporation. After a few days, dark green single crystals appeared that were collected by filtration and vacuum-dried. Yield: 0.12 g (55%). Anal. Calcd for C$_{14}$H$_{14}$N$_9$O$_2$SMn: C, 39.35; H, 3.30; N, 29.50. Found: C, 39.08; H, 3.17; N, 29.16. IR(KBr/cm^{-1}) dicyanamide: 2314s, 2298s, 2243s, 2188vs, and 2168vs. NO: 1353.

Crystal Structure Determination of [Mn^{II}(NIT-tz)(dca)$_2$] (1). Pertinent crystallographic data are summarized in Table 1. Diffraction data were collected on a Siemens P4 diffractometer in the

(14) Lamchen, M.; Wittig, T. W. *J. Chem. Soc. C* **1966**, 2300.
(15) Pascal, A. *Ann. Chim. Phys.* **1910**, *19*, 5.
(16) Ullman, E. F.; Call, L.; Osiecki, J. H. *J. Org. Chem.* **1970**, *35*, 3623.

Figure 1. ORTEP representation (40% thermal ellipsoids) of **1** with atom level schemes. The other end of each dca bridges four different metal centers. Symmetry code: A, 0.5 − *x*, 2 − *y*, *z* − 0.5; B, *x* − 0.5, 1.5 − *y*, 1 − *z*.

$\omega-2\vartheta$ scan mode at 293 K using graphite monochomated Mo Kα radiation having λ = 0.71073 Å. Three standard reflections were periodically monitored and showed no significant variation over data collection. The accurate unit cell was obtained by means of least-squares fitttings of 25 centered reflections. The intensity data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections were made from ψ-scans. A total of 1925 reflections were collected in the range 2ϑ = 4.38−50° with $-1 \leq h \leq 13$, $-1 \leq k \leq 15$, $-1 \leq l \leq 16$, all of which were independent (R_{int} = 0.0000) and used for structure determinations. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares methods based on F^2 using the programs SHELXTL-PLUS and SHELXL-93.[17] Neutral atom scattering factors were taken from standard source.[18] All non-hydrogen atoms were readily located and refined by anisotropic thermal parameters. The final least-squares refinements (R1) based on $I > 2\sigma(I)$ converged to 0.0386.

Results and Discussion

Description of Structure of [Mn^{II}(NIT-tz)(dca)$_2$] (1). An ORTEP representation of the coordination environment is shown in Figure 1, and the selected bond lengths and angles are listed in Table 2. The metal ion is hexacoordinated by the radical and dicyanamide anions. The radical behaves as a bidentate chelating ligand through one nitronyl nitroxide oxygen (O(1)) and the thiazole nitrogen (N(3)), while the other nitronyl nitroxide oxygen (O(2)) and the sulfur atom remain uncoordinated. The remaining four positions are occupied by the nitrile nitrogens of four dicyanamide ligands, the other end of each of which coordinates to four different manganese atoms; i.e., the metal ions are bridged by four single end-to-end dicyanamides to result in a three-dimensional architecture (vide infra). The geometry around the manganese atom is distorted octahedral. The best equatorial plane is defined by O(1), N(3), and two dca nitrogens (N(7) and N(6A)) with the deviation of ligand

(17) (a) *SHELXTL-PLUS*; Siemens Crystallographic Research Systems: Madison, WI, 1990. (b) Sheldrick, G. M. *SHELXL-93: A Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.
(18) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

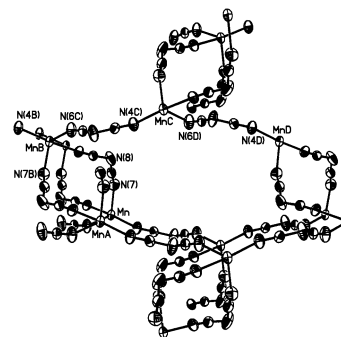**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for [Mn^{II}(NIT-tz)(dca)$_2$] (**1**)

Mn−O(1)	2.179(3)	C(12)−N(6)	1.113(7)
Mn−N(3)	2.286(4)	C(13)−N(7)	1.128(7)
Mn−N(4)	2.189(5)	C(14)−N(9)	1.135(7)
Mn−N(7)	2.159(5)	C(11)−N(5)	1.282(7)
Mn−N(6A)	2.188(5)	C(12)−N(5)	1.293(7)
Mn−N(9B)	2.221(5)	C(13)−N(8)	1.291(7)
C(11)−N(4)	1.129(7)	C(14)−N(8)	1.293(7)

O(1)−Mn−N(6A)	171.9(2)	N(4)−Mn−N(6A)	93.2(2)
N(3)−Mn−N(7)	173.5(2)	N(7)−Mn−N(6A)	93.8(2)
N(4)−Mn−N(9B)	171.5(2)	N(7)−Mn−N(9B)	95.2(2)
O(1)−Mn−N(4)	89.7(2)	N(6A)−Mn−N(9B)	90.6(2)
O(1)−Mn−N(7)	93.7(2)		
O(1)−Mn−N(9B)	85.5(2)	Mn−N(4)−C(11)	159.3(5)
O(1)−Mn−N(3)	80.09(14)	Mn−N(7)−C(13)	153.5(5)
N(3)−Mn−N(9B)	86.2(2)	Mn−N(6A)−C(12A)	157.7(6)
N(3)−Mn−N(6A)	92.6(2)	Mn−N(9B)−C(14B)	175.9(5)
N(3)−Mn−N(4)	86.1(2)	C(11)−N(5)−C(12)	125.8(6)
N(4)−Mn−N(7)	92.1(2)	C(13)−N(8)−C(14)	121.9(5)

Figure 2. Perspective view down the *a* axis to show the construction of three dimensions. The radical is deleted for clarity. The zigzag chain, −MnB−MnC−MnD−, propagates along the *c* direction. Symmetry code: Mn, *x*, *y*, *z*; MnA, 1 + *x*, *y*, *z*; MnB, 0.5 + *x*, 1.5 − *y*, 1 − *z*; MnC, 1 − *x*, *y* − 0.5, 1.5 − *z*; MnD, 0.5 + *x*, 1.5 − *y*, 2 − *z*.

Figure 3. Perspective view down the *a* axis to show the spiral network in the region of linking and cross-linking of the dca2. The radical and dca1 are deleted for clarity. The directions of axes are same as in Figure 2.

atoms and the metal centers being, respectively, 0.047 Å (average) and 0.016 Å. The axial positions are occupied by other two dca nitrogens, N(4) and N(9B). The four Mn−N(dca) bond lengths are slightly different [Mn−N(4) = 2.189(5) Å, Mn−N(7) = 2.159(5) Å, Mn−N(6A) = 2.188(5) Å, and Mn−N(9B) = 2.221(5) Å] and in the range observed for other Mn^{II}−dca systems.[4d,e,8b,d,e,11a,b] Regarding two metal−radical bond distances, while the Mn−O(1) separation (2.179(3) Å) is very close to Mn−N(dca), the Mn−N(3) distance (2.286(4) Å) is appreciably different. Again, the transoid and cisoid angles vary, respectively, from 171.9(2)° to 173.5(2)° and from 80.09(14)° to 95.2(2)° indicative of the distortion from O_h geometry.

One axial dca links with the metal ion in almost linear fashion with Mn−N(9B)−C(14B) angle of 175.9(5)°. The other three dca coordinates in a significantly bent way having Mn−N−C angles of 159.3(5)°, 157.7(6)°, and 153.5(5)°. The C≡N and C−N distances of both the two crystallographically different dca anions (N(4)C(11)N(5)C(12)N(6) (dca1) and N(7)C(13)N(8)C(14)N(9) (dca2)) are almost similar (Table 1). In addition, the C−N−C angles of dca1 (125.8(6)) and dca2 (121.9(5)) indicate the pseudo-C_{2v} symmetry of the dicyanamides.

The two N−O distances of the radical are very close with N(1)−O(1) = 1.284(5) Å and N(2)−O(2) = 1.266(6) Å. The O(1)N(1)C(4)N(2)O(2) moiety is almost planar; the maximum and minimum deviation of the atoms from this plane are 0.03 Å for O(1) and 0.006 Å for N(2), indicating the easy delocalization of the free electron within this moiety. The dihedral angle between the thiazole ring and the nitronyl nitroxide group is 10.2°.

For both dca1 and dca2, one end binds in the equatorial position and the other end in the axial position of another metal ion to form an interesting example of three-dimensional network. A perspective view down the *a* axis is shown in Figure 2 to show the construction of the three-dimensional network. The two dca1 (linked to MnC) species, which are in cis positions, bridge two metal ions (MnB and MnD) to result a one-dimensional zigzag chain. The chain propagates along the *c* axis. The alternate metal ions of this chain lie in the same plane keeping the other metal ions up for one set
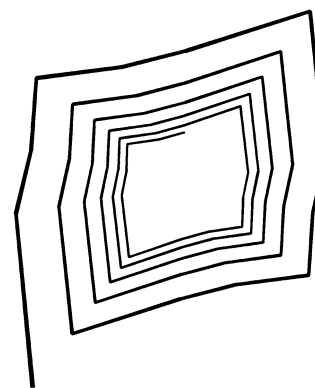
or down for another set of alternate members. These one-dimensional chains are stitched by the two dca2 species, which are also in cis positions, to generate the second and third dimensions. One dca2 of a metal ion (MnB) of a zigzag chain links to the adjacent metal center (MnA) in the same *bc* plane of the neighboring chain. For the successive metal centers, this type of linking takes place in opposite directions to afford the second dimension (vide infra) of the structure. The third dimension is achieved by the cross-linking of the second dca2 (of MnB) to the immediate lower member (Mn) of the metal ion (MnA) to which the first dca2 binds. Thus, while the cross-linking of one dca2 generates the third dimension, both the linking of one dca2 and cross-linking of another dca2 may be considered to be responsible for the construction of the second dimension. The region of linking and cross-linking of dca2 creates, as viewed along the *a* axis (Figure 3), an interesting spiral network and diamond-shaped channels (∼20.7 Å^2). Again, this bridging region looks helical when viewed down the *b* axis. Due to the spiral propagation down the *a* axis, the loops of one helical chain become alternately up and down with respect to the neighboring member.

An extended view of the structure is shown in Figure 4. The packing can be considered as the repetition of average hexagonal spaces that are occupied by the diamond-shaped channels and the radicals, which are inclined by 26.9° with the *ab* plane. The separations between the metal ions along
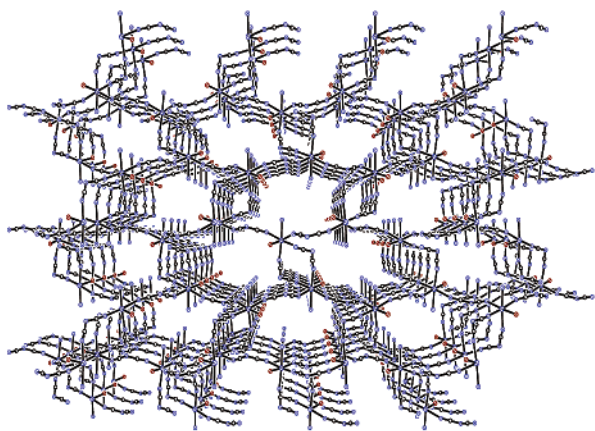
Figure 4. Packing diagram down the *a* axis. Only the donor centers of the radical are shown. The directions of axes are same as in Figure 2.
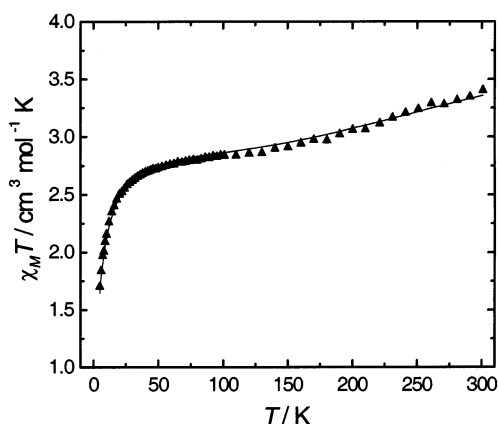

Figure 5. Experimental (▲) and calculated (—) $\chi_M T$ vs T plots for [Mn^{II}-(NIT-tz)(dca)$_2$] (**1**).

the three directions are, respectively, 11.015 Å (Mn⋯MnA, Figure 2), 7.945 Å (MnA⋯MnB, Figure 2), and 8.654 Å (MnB⋯MnC, Figure 2). The nitronyl nitroxide groups are well separated with the closest O(1)⋯O(1), O(2)⋯O(2), and O(1)⋯O(2) being, respectively, 11.015, 11.015, and 7.588 Å.

Magnetic Property. Variable-temperature (5−300 K) magnetic behavior at fixed field strength of 1 T for the title compound is shown in Figure 5 in the form of a $\chi_M T$ versus T plot. The $\chi_M T$ value at 300 K is 3.40 cm^3 mol^{-1} K, which is significantly lower than the calculated value (4.75 cm^3 mol^{-1} K, $g = 2$) of two uncoupled spins of $s = {}^5/_2$ and $s = {}^1/_2$. On lowering the temperature, $\chi_M T$ decreases gradually to 2.84 cm^3 mol^{-1} K at 110 K, passes through a plateau in the temperature range 110−40 K ($\chi_M T = 2.70$ cm^3 mol^{-1} K at 40 K), and then rapidly decreases up to 5 K where its value is 1.70 cm^3 mol^{-1} K. The profile indicates the existence of an antiferromagnetic interaction in **1**. As the nitronyl nitroxide groups are well separated, there exist two possible kinds of exchange interactions: metal−radical and dca bridged metal−metal. Between these, the latter pathway is known to mediate only weak antiferromagnetic interactions,[8−12] while the radical−metal coupling depends on several factors and is expected to be much higher than the magnitude of interactions through dca. Thus, the exchange can be logically modeled as the two-spin system of $s = {}^5/_2$ and $s = {}^1/_2$ with

the metal−metal interactions taken as the intermolecular interaction. Least-squares fitting of the experimental data with the theoretical equation derived from the Hamiltonian $\mathbf{H} = -2J\mathbf{S_1 \cdot S_2} - 2zJ'\langle\mathbf{S}\rangle S$, where the last term in the Hamiltonian indicates the molecular field approximation to account for the intermolecular interactions, leads to $J = -73$ cm^{-1}, $g = 1.99$, and $zJ' = -0.7$ cm^{-1}; the agreement factor defined as $[\Sigma\{(\chi_M T)_{obsd} - (\chi_M T)_{calcd}\}^2/\Sigma(\chi_M T)_{obsd}{}^2]$ is 1.07×10^{-2}.

Now, as the number (z) of neighboring metal centers of a manganese(II) ion is 4, the value of J' becomes 0.175 cm^{-1}. Hence, the magnitude of antiferromagnetic coupling through each dca bridge can be considered as -0.175 cm^{-1} which is in the range (-0.06 to -0.17 cm^{-1}) observed in other dca bridged manganese(II) systems.[4d,e,8b,d,e,11a,b]

The antiferromagnetic interaction in **1** is weaker than that observed in the manganese(II)−nitronyl nitroxide complexes where only the nitronyl oxygens are bound to the metal center.[1b] However, similar interactions are known in a few examples where the metal ions are chelated by nitronyl oxygens and other donor centers of the radicals.[1h−j] The difference of the magnitudes of the exchange integrals of two types of systems is basically dependent on the extent of overlap of the SOMO π^* orbital of the radical with the magnetic orbitals of metal ions. As the axis of the π^* orbital lies perpendicular to the imidazoline plane,[19] more efficient overlap and a stronger interaction are possible if the dihedral angle (δ) between M−O−N and imidazoline planes become 90°. When nitronyl nitroxide coordinates only through nitronyl oxygens, the δ values become close to 90° resulting in exchange integrals in the range -150 to -200 cm^{-1}.[1b] If the radicals chelate to the metal ion, the δ value decreases in most of the cases, and as a result, the antiferromagnetic interaction becomes weaker as observed in [Mn(NIT-R)$_3$] (**2**: R = 2-pyridyl; $\delta = 46.4°, 44.3°, 35.2°$; $J = -88$ cm^{-1}. **3**: R = benzimidazole; $\delta = 23.9°, 35.6°, 40.6°$; $J = -79$ cm^{-1}. **4**: R = imidazole; $\delta = 9.6°, 31.3°, 18.9°$; $J = -53$ cm^{-1}),[1h] [Mn(NIT-2-pyridyl)$_2$(Cl)$_2$] (**5**: $\delta = 48°$; $J = -79$ cm^{-1}),[1i] [Mn(NIT-2-pyridyl)(hfac)$_2$] (**6**: $\delta = 42°$; $J = -65$ cm^{-1}),[1i] and [Mn(2,6-NITpy)$_2$] (**7**: $\delta = 54.7°, 59.0°, 75.8°$, 64.9°; $J = -83$ cm^{-1}).[1j] In contrast, in a manganese(II) compound of a phosphine oxide substituted radical, in spite of the chelation by the nitronyl and phosphine oxide oxygens, the δ value is 94.5° which results, expectedly, in the J value (-106.5 cm^{-1}) in the higher range.[1k] Now, the δ value of the title compound (**1**) is 36.7°. Thus, the antiferromagnetic interaction of -73 cm^{-1} is right in the line of theoretical prediction as well as of the reported examples.

Conclusions. A new nitronyl nitroxide radical has been introduced in the field of molecular magnetism. The reported coordination complex is the first example to have the three-dimensional structure in the metal ion−nitronyl nitroxide (or imono nitroxide)−pseudohalide family. The three-dimensional structure is achieved by the novel linking and cross-linking of the metal ions by the dicyanamides. Crystal engineering leads to the existence of spiral networks, helical

(19) Zheludev, A.; Barone, V.; Bonnet, M.; Delley, B.; Grand, A.; Ressouche, E.; Rey, P.; Subra, R.; Schweizer, J. *J. Am. Chem. Soc.* **1994**, *116*, 2019.

and zigzag chains, and dimond-shaped channels inside the structure. The Mn^{II}−radical magnetic interaction of −73 cm^{-1} is another example of a rare number of compounds where the antiferromagnetic interaction is decreased by the coordination of chelating nitroxides. Isolations and studies of the exchange behaviors of more compounds of this type of metal ion−chelating nitroxides, particularly, with a single δ value, are expected to provide an excellent $-J$ versus δ correlation similar to the well-known linear dependences of couplings with bridge angle or dihedral angles in the 3d− 3d bimetallic systems.[1a,20]

Supporting Information Available: Crystallographic data in CIF format and figure to demonstrate the helical network down the *b* axis. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025768U

(20) Mohanta, S.; Nanda, K. K.; Thompson, L. K.; Flörke, U.; Nag, K. *Inorg. Chem.* **1998**, *37*, 1465.