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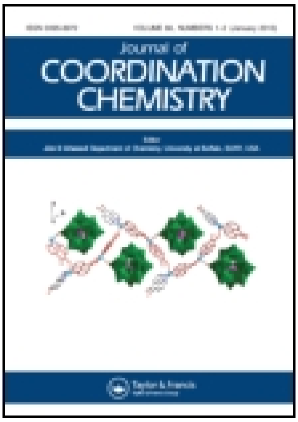

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structure, spectroscopic study, and magnetic behavior of the first dinuclear Mn(II) complex of hydrazone-based ligand-containing dicyanamide bridging groups

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Accepted author version posted online: 28 Oct 2013.Published online: 26 Nov 2013.

To cite this article: Rahman Bikas, Hassan Hosseini-Monfared, Lesław Sieroń & Angel Gutiérrez (2013) Synthesis, crystal structure, spectroscopic study, and magnetic behavior of the first dinuclear Mn(II) complex of hydrazone-based ligand-containing dicyanamide bridging groups, Journal of Coordination Chemistry, 66:22, 4023-4031, DOI: 10.1080/00958972.2013.858811

To link to this article: http://dx.doi.org/10.1080/00958972.2013.858811

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 22, 4023–4031, http://dx.doi.org/10.1080/00958972.2013.858811

Synthesis, crystal structure, spectroscopic study, and magnetic behavior of the first dinuclear Mn(II) complex of hydrazone-based ligand-containing dicyanamide bridging groups

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(*Received 11 August 2013; accepted 10 October 2013*)

A new dinuclear complex of manganese(II), $[Mn(L)(\mu_{1,5}\text{-dca})(CH_3OH)]_2$ (**1**), with dicyanamide anion and (*E*)-3-hydroxy-*N*′-(pyridin-2-ylmethylene)-2-naphthohydrazide (HL) was synthesized. The complex was characterized by elemental analyzes, spectroscopic methods, X-ray diffraction, and magnetic susceptibility studies. Two manganese ions in the complex were connected by two bridging dicyanamide ligands in a symmetric end-to-end ($\mu_{1,5}$-dca) fashion. The presence of intramolecular hydrogen bonding in the mononegative naphthohydrazone (L^-) affects keto-enol tautomerism and the ligand coordinates to manganese(II) in the keto-form. Magnetic measurements showed an antiferromagnetic interaction between adjacent manganese ions in the dimer.

Keywords: Hydrazone ligands; Dinuclear complex; X-ray crystal structure; Manganese complex; Dicyanamide bridge

1. Introduction

Design and synthesis of transition metal complexes with dicyanamide (dca) have attracted great attention and this has gradually become one of the most active fields in inorganic and coordination chemistry [1]. Due to the presence of three potential donor centers and remarkably versatile coordination modes, dca is an attractive bridging ligand for the synthesis of di- and multinuclear complexes [2]. The versatility of dicyanamide as a bridging ligand has been illustrated by its six structurally characterized coordination modes [3]. As a bridging ligand, the dca anion can bind metal ions in μ_2–1,5-dca [4], μ_2–1,3-dca [5], μ_3–1,1,5-dca [6], μ_3–1,3,5-dca [7], μ_4–1,1,3,5-dca [8], and μ_5–1,1,3,5,5-dca [9] coordination modes, among which the μ_2–1,5-dca is the most common. Dicyanamide is also an important magnetic coupler [3]. Several studies done on magnetic behavior of dicyanamide complexes indicate it can mediate weak interactions between paramagnetic metal centers [10],

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*Corresponding author. Email: bikas@znu.ac.ir nonetheless, a few multidimensional dicyanamide-bridged compounds exhibit long-range magnetic ordering through spin-canted antiferromagnets or ferromagnets [3, 11]. It is now obvious that the change in the coordination geometry around the metal center has quite significant effect on the magnetic nature [12]. There are several reports which illustrate that geometry and magnetic properties of complexes depend on the nature of the co-ligand [13]. Therefore, it may be noted that utilization of a new organic ligand may result in new types of topologies and interactions in metal-dicyanamide complexes. In this way, the chemistry of aroylhydrazones, R–CO–NH–N = CR′R″ (R, R′, and R″ = H, alkyl, and aryl), has attracted increasing interest due to their chelating ability and their applications in coordination chemistry [14], analytical chemistry [15], bioinorganic chemistry [16], and use in the treatment of several diseases [17]. Hydrazone ligands create environment similar to biological systems usually by coordination through oxygen and nitrogen [18]. Their metal complexes have also found applications in various chemical processes, such as catalysis [19] and magnetic materials [20]. Some dinuclear complexes containing hydrazone ligands show exchange coupling like those found in binuclear metalloproteins [21].

To the best of our knowledge and according to the reported structures in CCDC database, the crystal structures of metal complexes containing mixed ligands of hydrazone Schiff base and dicyanamide are rare and only three examples of this kind of complexes have been reported [22]; all of them are copper(II) complexes. Continuing our studies on the preparation of transition metal complexes with hydrazone-based ligands [21, 23] and considering that the organic ligand may affect the magnetic and physical properties of dicyanamide-based complexes, we have been interested in employing mixed hydrazone/dicyanamide ligands to prepare new manganese complexes. In thisarticle, we describe the synthesis, structure, and magnetic behavior of the first dinuclear Mn(II) complex using mixed hydrazone and dicyanamide ligands.

2. Experimental

2.1. *Materials and instrumentations*

All the starting chemicals were commercially available reagents and used without purification. The ligand (*E*)-3-hydroxy-*N*′-(pyridin-2-ylmethylene)-2-naphthohydrazide (HL) was synthesized and characterized according to the reported procedure [24]. IR spectra were recorded as KBr disks with a Bruker FT-IR spectrophotometer. UV–vis spectra of solution were recorded on a thermo spectronic, Helios Alpha spectrometer. ^{1}H and ^{13}C NMR spectra of ligand in DMSO-d$_6$ solution were recorded on a Bruker 250 MHz spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. Magnetic experiments were made on polycrystalline samples using a SQUID magnetometer MPMS XL-5 manufactured by Quantum Design. The temperature dependence of the magnetization in the range 2 and 300 K was recorded using a constant magnetic field of 0.10 T. The experimental data have been corrected for the magnetization of the sample holder (gelatine) and for atomic diamagnetism as calculated from the known Pascal's constants.

2.2. *Synthesis of [Mn(L)($\mu_{1,5}$-dca)(CH_3OH)]$_2$ (1)*

[Mn(L)($\mu_{1,5}$-dca)(CH_3OH)]$_2$ (**1**) was synthesized according to reported procedure [25]. The naphthohydrazone ligand, HL (0.305 g, 1.0 mmol), was dissolved in methanol (30 mL) followed by the addition of $MnCl_2 \cdot 4H_2O$ (0.22 g, 1.1 mmol), and sodium dicyanamide (0.18 g, 2 mmol); the resulting solution was gently refluxed for 6 h. After cooling, the solid was filtered off, washed with cooled methanol, and dried at 60 °C. To isolate single crystals of **1**, the above-mentioned substrates were placed in the main arm of a branched tube. Solvent was carefully added to fill the arms, the tube was sealed and the reagents-containing arm was immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After four days, crystals were deposited in the cooler arm, which were filtered off, washed with methanol, and air dried. Yield: 85% (0.388 g). Anal. Calcd for $C_{42}H_{36}Mn_2N_{12}O_6$ (MW = 914.71): C, 55.15; H, 3.97; N, 18.38; Mn, 12.01. Found: C, 55.11; H, 4.00; N, 18.41; Mn, 12.09%. FT-IR (KBr, cm^{-1}): 3400 (w, br), 2941 (w), 2844 (w), 2308 (s), 2235 (s), 2186 (vs), 1632 (s), 1595 (s), 1574 (m), 1531 (vs), 1469 (s), 1456 (s), 1449 (s), 1378 (s), 1364 (vs), 1328 (s), 1307 (m), 1240 (m), 1221 (m), 1160 (m), 1148 (m), 1046 (m), 1024 (s), 911 (m), 868 (m), 779 (s), 747 (s), 739 (s), 677 (m), 633 (m), 525 (m), 512 (m), 479 (s), 409 (s). UV–vis spectrum in CH_3OH [λ_{max}, (ε, M^{-1} cm^{-1}), $c = 2.5 \times 10^{-5}$]: 220 (78 200), 360 nm (33 800).

2.3. *X-ray crystallography*

X-ray diffraction data for **1** was collected at 291 K by the ω-scan technique on a KUMA KM4CCD κ-geometry diffractometer equipped with a Sapphire CCD detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Data integration and numerical absorption corrections were carried out with the CrysAlis program [26]. The structure was solved by direct methods by using SHELXS-97 [27]. All the non-hydrogen

Table 1. Crystallographic data of **1**.

Formula	$C_{42}H_{36}Mn_2N_{12}O_6$
Formula weight	914.71
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.7144(7)
b (Å)	17.226(2)
c (Å)	16.0274(17)
β (°)	103.818(11)
V (Å^3)	2068.2(4)
Z	2
D_x (g cm^{-3})	1.469
F (0 0 0)	940
μ (mm^{-1})	0.675
Crystal shape (color)	Block (Red)
Crystal size (mm)	0.20 × 0.20 × 0.10
θ Range (°)	1.8 – 36.4
$h/k/l$ range	$-9 \rightarrow 9$ $-20 \rightarrow 20$ $-18 \rightarrow 19$
Reflections	
Collected	27175
Unique (R_{int})	3627 (0.030)
With $I > 2\sigma(I)$	3068
$R(F)$ [$I > 2\sigma(I)$]	$R_1 = 0.0288$, w$R_2 = 0.0746$
$wR(F^2)$ [all data]	0.0723
Goodness of fit	1.02
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.25/−0.30

atoms were refined anisotropically by full-matrix least-squares based on F^2 using SHELXL-97 [27], and the complete set of reflections. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (0.039P)^2 + 0.6113P]$, where $P = (F_o^2 + 2F_c^2)/3$. The hydroxy H-atom was refined freely. All the remaining hydrogens were placed in calculated positions and were refined as "riding" on their parent [C_{sp2}–H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C_{sp2})$ and C_{sp3}–H = 0.96 Å, $U_{iso}(H) = 1.5U_{eq}(C_{sp3})$]. Methyl groups were refined as idealized disordered over two sites rotated by 60° from one another. The final geometrical calculations were mainly performed within PLATON [28]. Crystallographic data are listed in table 1.

3. Results and discussion

3.1. *Syntheses and spectroscopy*

The reaction of 3-hydroxy-2-naphthoic acid hydrazide with 2-acetylpyridine in methanol gave the desired dissymmetric Schiff base (HL) in excellent yield and purity. The complex $[Mn(L)(\mu_{1,5}\text{-dca})(CH_3OH)]_2$ (**1**) of this ligand was prepared in high yield from the reaction of $HL/MnCl_2\cdot 4H_2O/NaN(CN)_2$ with molar ratios 1.0 : 1.1 : 2.0 in a branched tube and using methanol as solvent. Two tautomeric structures of the keto and enol forms are expected for HL. The infrared spectrum of HL (figure S1) displays the characteristic bands at 3262, 1646, and 1599 cm^{-1}, assigned, respectively, to υ(N–H), υ(C=O), and υ(N=C) of the amide of the free Schiff base. The presence of υ(OH) as a weak band at 3449 cm^{-1} suggests this group is involved in hydrogen bonding. The N–H band disappears in IR spectra of **1** (figure S2), suggesting the elimination of the amide hydrogen upon coordination to manganese. This is supported by the 13 cm^{-1} shift of υ(C=O) to lower frequencies. Amide deprotonation without enolization is in contrast with reported studies of aroylhydrazone complexes [19, 21, 23, 29] but is in good agreement with our previous observation in copper(II) complexes using the same ligand [24]. Further studies with single crystal X-ray studies also confirmed the coordination of L$^-$ as =N–N–C(=O)– like that observed in the copper(II) complexes. Absorptions at 1595 cm^{-1} can be assigned to the imine C=N stretch of the coordinated hydrazone [30]. IR spectra of **1** show the characteristic stretches of dicyanamide. The solid state of **1** depicts a very strong band at 2186 cm^{-1} and two medium to strong bands at 2235 and 2308 cm^{-1} which were attributed to the υ_{sym}(CN), υ_{asym}(CN), and $\upsilon_{sym} + \upsilon_{asym}$ (CN) modes, respectively. The shift to higher wavenumbers of dca peaks in **1** when compared to those of the free dicyanamide (2181, 2229 and 2287 cm^{-1}) is consistent with coordination of dca in the complex. The υ_{asym}(C–N) stretching frequency and the υ_{sym}(C–N) stretch occur at 1364 and 911 cm^{-1}, respectively. The observed IR bands are in agreement with literature data for coordinated dca [31]. A very broad absorption at 3400 cm^{-1} (O–H stretch) in the infrared spectrum of **1** is due to the naphtholic O–H and the presence of coordinated methanol, both involved in hydrogen bonding.

Electronic spectra of **1** (light red) and HL (colorless) in MeOH solution are shown in figure S3. The hydrazone has strong bands at 230 and 311 nm. Based on their extinction coefficients they are assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Shifts of the bands in complex relative to HL indicate coordination of ligand to Mn(II). For **1**, the higher energy band at 360 nm is due to coordinated L$^-$, O(σ) → Mn(II) charge transfer transition. The other higher energy intense transition at 220 nm is due to intraligand $\pi \rightarrow \pi^*$ and charge transfer transitions.

3.2. *X-ray structure of [Mn(L)($\mu_{1,5}$-dca)(CH_3OH)]$_2$ (1)*

The molecular structure of [Mn(L)($\mu_{1,5}$-dca)(CH_3OH)]$_2$ (**1**) has been determined by X-ray crystallography. A plot of the dimeric unit with atom numbering scheme is shown in figure 1 and selected bond lengths and angles are collected in the figure caption. The structural analysis reveals that the crystals of **1** are built of neutral binuclear units containing double μ_2–1,5-N(CN)$_2$ bridging groups. The manganese in **1** is six-coordinate, as *cis*-[Mn(O)(ONN)(N)$_2$], with oxygen (O1) and two nitrogens (N1 and N2) provided by the Schiff base, O3 from the methanol and two nitrogens (N4 and N6) from two end-to-end bridging μ_2–1,5-dca ligands. The overall geometry around manganese(II) in **1** is best described as slightly distorted octahedral. The aroylhydrazone Schiff base ligand forms a basal plane (equatorial plane) together with nitrogen from one dicyanamide. One axial position is occupied by nitrogen from the second dicyanamide bridge and methanol is coordinated to the remaining axial position. Two manganese(II) cations and two bridging dicyanamide groups create a 12-membered Mn–(NCNCN)$_2$–Mn centrosymmetric dimeric ring. In this dimeric unit the Mn···Mn distance is 7.4683(9) Å, close to other reported Mn(II) complexes of $\mu_{1,5}$-dicyanamide bridges [32]. The Mn–O and Mn–N distances are close to those found in other Mn(II) complexes with hydrazone-based N_2O-donors [29]. The dicyanamide bridges show approximately symmetric N≡C–N–C≡N distances (*av.* C≡N = 1.131 Å and *av.* C–N = 1.287 Å) and the C20–N5–C21$^{(-x+2,\ -y+2,\ -z+1)}$ angle is 122.20(18)°, typical for dicyanamide ligand [33].

The hydrazone is monoanionic and hydrogen of N–H has been eliminated during complexation but the ligand has coordinated in its keto form which can be verified from C8=O1 (1.257(2) Å) and C8–N3 (1.336(2) Å) bond lengths. For aroylhydrazones in the enol form the bond lengths of C–O and C=N are 1.29–1.31 and 1.29–1.32 Å, respectively. These values for aroylhydrazones in the keto form are 1.24–1.28 and 1.32–1.35 Å, respectively [24]. Comparison of these values indicates in **1** the C=O and C–N bond distances are in agreement with L^- in the keto form. This complex shows a strong internal hydrogen bond of the O–H···N type for coordinated L^- (table 2). The intramolecular hydrogen bond reinforces deprotonation of N–H of amide and then stabilizes it in the keto form. Appearance of *υ*(C=O) supports the presence of coordinated L^- in keto form [34]. This finding is in agreement with our observation in copper(II) complexes using the same ligand [24]. The intermolecular O–H···O hydrogen bonds, involving the naphtholic oxygen as an acceptor, link the molecules into a 1-D polymeric chain running along the *c* axis (table 2, figure 2).

3.3. *Magnetic studies*

The temperature dependence of χT per manganese dimer for **1** is shown in figure 3. The room temperature value of 9.16 cm^3 K mol^{-1} (8.56 β) fits well with the expected value of 8.75 cm^3 K mol^{-1} for two uncoupled high spin manganese(II), $S = 5/2$, ions. On cooling, this value remains approximately constant to 80 K and then decreases to a minimum of

Table 2. Hydrogen-bond geometry (Å, °).

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O2–H20···N3	0.92(3)	1.61(3)	2.4688(18)	155(3)
O3–H30···O2^i	0.79(2)	1.90(2)	2.6730(19)	169(2)

Note: Symmetry code: $i = -x+2, -y+2, -z$.

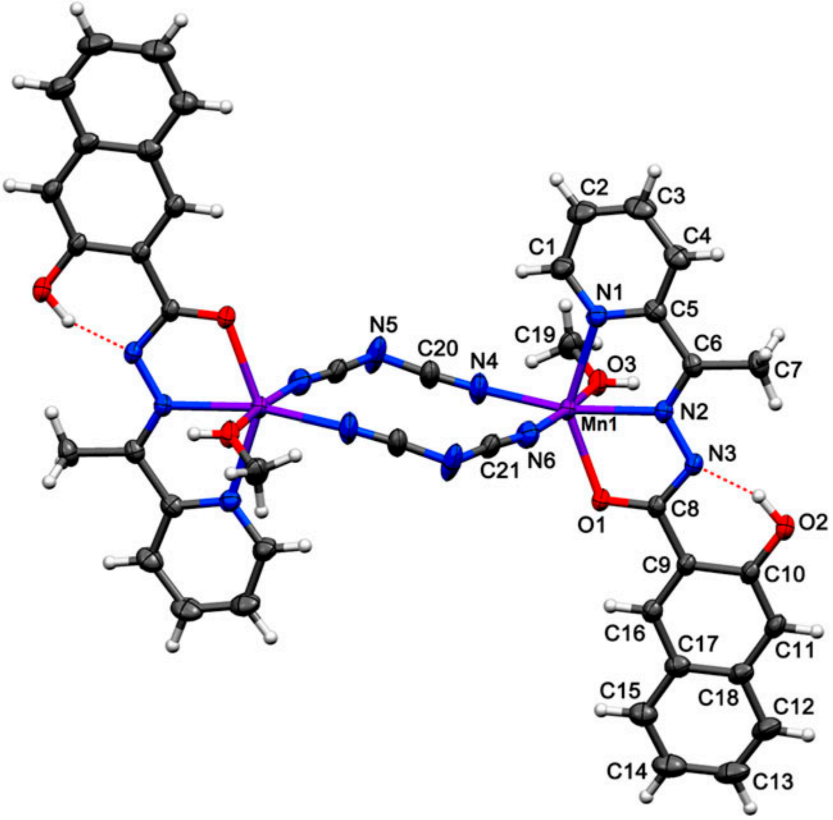

Figure 1. Molecular structure of **1** together with atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Intermolecular hydrogen bonds are shown as dashed lines. Selected interatomic bond distances (Å) and angles (°): Mn1–O1 2.1642(12), Mn1–O3 2.2378(14), Mn1–N1 2.2910(16), Mn1–N2 2.1914(13), Mn1–N4 2.1422(17), Mn1–N6 2.2073(17), O1–C8 1.257(2), N3–C8 1.336(2), N4–C20 1.132(2), N5–C20 1.280(2), N5–C21^i 1.294(2), N6–C21 1.130(2), O1–Mn1–O3 88.63(5), O1–Mn1–N1 142.71(5), O1–Mn1–N2 72.31(5), O1–Mn1–N4 116.87(7), O1–Mn1–N6 93.78(6), O3–Mn1–N1 88.48(5), O3–Mn1–N2 86.14(5), O3–Mn1–N4 85.53(6), O3–Mn1–N6 173.43(6), N1–Mn1–N2 70.40(5), N1–Mn1–N4 99.94(7), N1–Mn1–N6 93.27(6), N2–Mn1–N4 167.41(6), N2–Mn1–N6 100.41(6), N4–Mn1–N6 87.93(6), N5^i–C21–N6 173.7(2), where $i = -x+2, -y+2, -z+1$.

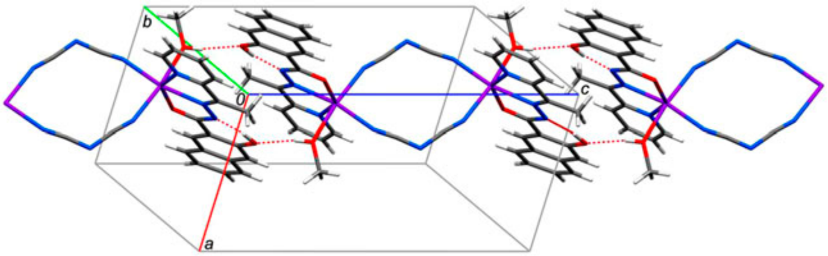

Figure 2. The 1-D polymeric chain linking molecules of **1** via hydrogen bonds (dashed lines) and running along the *c* axis.

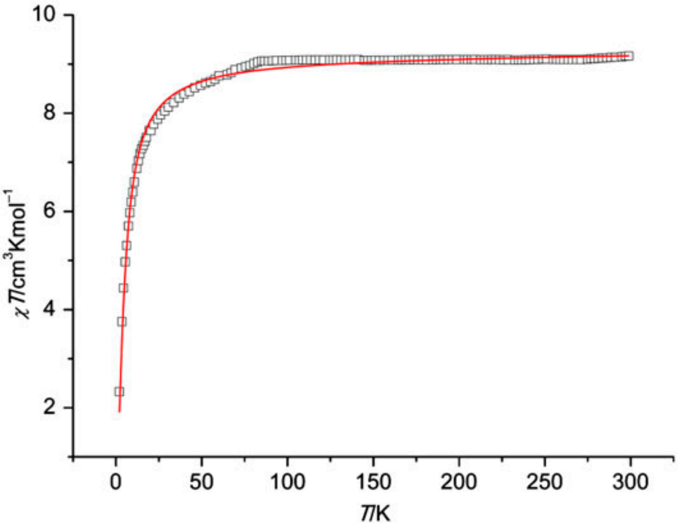

Figure 3. Temperature dependence of χT for **1**. The solid lines represent fits using equation and parameters described in the text.

2.33 cm^3 K mol^{-1} (4.31 β) at 2 K. This behavior is compatible with an antiferromagnetic coupling exchange between manganese(II) ions that form the dimers observed in the crystal structure. Accordingly, the experimental data were fitted to the Heisenberg dimer model for two interacting $S = 5/2$ ions. The spin Hamiltonian used was $H = -2\ J{\cdot}S_1{\cdot}S_2$. The best fit was obtained for $g = 2.047(3)$ and $J = -0.347(5)$ cm^{-1} with $R^2 = 0.991$. The fit indicates a small intradimer antiferromagnetic coupling as expected from the crystal structure and considers negligible any other exchange interaction between adjacent dimers.

4. Conclusion

A new dinuclear complex of manganese(II), $[Mn(L)(\mu_{1,5}\text{-dca})(CH_3OH)]_2$ (**1**), with dicyanamide and (*E*)-3-hydroxy-*N*′-(pyridin-2-ylmethylene)-2-naphthohydrazide (HL) was synthesized and characterized. X-ray analysis indicated two metal centers in the complex were connected by two bridging dicyanamides in a symmetric end-to-end ($\mu_{1,5}$-dca) fashion. The presence of intramolecular O–H···N hydrogen bonding in the mononegative naphthohydrazone ligand (L^-) affects keto-enol tautomerism and ligand coordinates to the metal ion in the keto-form. Magnetic measurements showed a small intradimer antiferromagnetic coupling between adjacent manganese ions.

Acknowledgements

The authors are grateful to the University of Zanjan, Lodz University of Technology and Universidad Complutense de Madrid (group 921508) for financial support of this study.

Supplemental data

Supplementary data to this article can be found online. Further details of the structure determination are available on request from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk) by quoting the depository number CCDC 931362 (http://www.ccdc.cam.ac.uk). Supplemental data for this article can be accessed http://dx.doi.org/10.1080/00958972.2013.858811.

References

[1] (a) S.-S. Qian, M. Zhang, Y.-N. Wang, F.-Y. Tian, L. Liu, Z.-L. You, H.-L. Zhu. *J. Coord. Chem.*, **66**, 1006 (2013); (b) Kafeel Ahmad Siddiqui. *J. Coord. Chem.*, **65**, 4168 (2012); (c) T.-F. Liu, Z. Bao, L.-L. Li. *J. Coord. Chem.*, **64**, 1063 (2011).
[2] (a) G. Marinescu, A.M. Madalan, S. Shova, M. Andruh. *J. Coord. Chem.*, **65**, 1539 (2012); (b) H.-Y. Liu, H.-Y. Wang, Y.-H. Shi. *J. Coord. Chem.*, **64**, 2859 (2011); (c) Z.-W. Li, P.-P. Yang, X.-L. Wang, L.-C. Li. *J. Coord. Chem.*, **63**, 1538 (2010).
[3] S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003).
[4] (a) X. Zhu, K. Liu, Y. Yang, B.-L. Li, Y. Zhang. *J. Coord. Chem.*, **62**, 2358 (2009); (b) S.-W. Wang, Y.-M. Zhang, B.-L. Li, Y. Zhang. *J. Coord. Chem.*, **59**, 2859 (2006).
[5] E. Colacio, I.B. Maimoun, F. Lloret, J. Suárez-Varela. *Inorg. Chem.*, **44**, 3771 (2005).
[6] Y.-J. Shi, L.-H. Li, Y.-Z. Li, X.-T. Chen, Z. Xue, X.-Z. You. *Polyhedron*, **22**, 917 (2003).
[7] M. Wriedt, C. Näther. *Dalton Trans.*, 886 (2011); (b) H.-L. Sun, S. Gao, B.-Q. Ma, G. Su. *Inorg. Chem.*, **42**, 5399 (2003).
[8] Y.M. Chow, D. Britton. *Acta Cryst.*, **B31**, 1934 (1975).
[9] Y.-J. Shi, X.-T. Chen, Y.-Z. Li, Z. Xue, X.-Z. You. *New J. Chem.*, **26**, 1711 (2002).
[10] M. Biswas, G.M. Rosair, G. Pilet, S. Mitra. *Inorg. Chim. Acta*, **360**, 695 (2007).
[11] (a) M.R. Pederson, A.Y. Liu, T. Baruah, E.Z. Kurmaev, A. Moewes, S. Chiuzbaian, M. Neumann, C.R. Kmety, K.L. Stevenson, D. Ederer. *Phys. Rev. B*, **66**, 014446 (2002); (b) P. Talukder, S. Shit, A. Sasmal, S.R. Batten, B. Moubaraki, K.S. Murray, S. Mitra. *Polyhedron*, **30**, 1767 (2011); (c) C.R. Kmety, J.L. Manson, S. McCall, J.E. Crow, K.L. Stevenson, A.J. Epstein. *J. Magn. Magn. Mater.*, **248**, 52 (2002).
[12] (a) Z. Shen, J.L. Zuo, S. Gao, Y. Song, C.M. Che, H.K. Fun, X.Z. You. *Angew. Chem. Int. Ed.*, **39**, 3633 (2000); (b) Z.D. Wang, W. Han, F. Bian, Z.Q. Liu, S.P. Yan, D.Z. Liao, Z.H. Jiang, P. Cheng. *J. Mol. Struct.*, **733**, 125 (2005).
[13] (a) A.M. Kutasi, S.R. Batten, B. Moubaraki, K.S. Murray. *J. Chem. Soc., Dalton Trans.*, 819 (2002); (b) P. Jensen, S.R. Batten, B. Moubaraki, K.S. Murray. *Chem. Commun.*, 793 (2000).
[14] Y.-M. Cui, Y. Wang, Y.-J. Cai, X.-J. Long, W. Chen. *J. Coord. Chem.*, **66**, 2325 (2013).
[15] L.N. Suvarapu, Y.K. Seo, S.O. Baek, V.R. Ammireddy. *Eur. J. Chem.*, **9**, 1288 (2012).
[16] P. Chatterjee, O.P. Shrivastava, L.B.V. Agarwala. *J. Inorg. Biochem.*, **36**, 246 (1989).
[17] (a) D.R. Richardson, P. Ponka. *Am. J. Hematol.*, **58**, 299 (1988); (b) D.S. Kalinowski, P.C. Sharpe, P.V. Bernhardt, D.R. Richardson. *J. Med. Chem.*, **51**, 331 (2008).
[18] L.S. Vojinović-Ješić, V.I. Češljević, G.A. Bogdanović, V.M. Leovac, K.M. Szécsényi, V. Divjaković, M.D. Joksović. *Inorg. Chem. Commun.*, **13**, 1085 (2010).
[19] H. Hosseini-Monfared, S. Kheirabadi, N.A. Lalami, P. Mayer. *Polyhedron*, **30**, 1375 (2011).
[20] P.-H. Lin, S. Gorelsky, D. Savard, T.J. Burchell, W. Wernsdorfer, R. Clerac, M. Murugesu. *Dalton Trans.*, 7650 (2010).
[21] R. Bikas, H. Hosseini-Monfared, G. Zoppellaro, R. Herchel, J. Tucek, A.M. Owczarzak, M. Kubicki, R. Zboril. *Dalton Trans.*, 2803 (2013).
[22] (a) S. Banerjee, S. Sen, S. Basak, S. Mitra, D.L. Hughes, C. Desplanches. *Inorg. Chim. Acta*, **361**, 2707 (2008); (b) V.A. Milway, S.M.T. Abedin, L.K. Thompson, D.O. Miller. *Inorg. Chim. Acta*, **359**, 2700 (2006); (c) S. Sen, S. Mitra, D.L. Hughes, G. Rosair, C. Desplanches. *Inorg. Chim. Acta*, **360**, 4085 (2007).
[23] (a) H. Hosseini-Monfared, R. Bikas, P. Mayer. *Inorg. Chim. Acta*, **363**, 2574 (2010); (b) R. Bikas, H. Hosseini-Monfared, T. Lis, M. Siczek. *Inorg. Chem. Commun.*, **15**, 151 (2012).
[24] H. Hosseini-Monfared, H. Falakian, R. Bikas, P. Mayer. *Inorg. Chim. Acta*, **394**, 526 (2013).
[25] K.S. Banu, S. Mondal, A. Guha, S. Das, T. Chattopadhyay, E. Suresh, E. Zangrando, D. Das. *Polyhedron*, **30**, 163 (2011).
[26] Xcalibur CCD System. *CrysAlis Software System, v. 1.171*, Oxford Diffraction, Ltd., Abingdon, England (2010).
[27] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[28] A.L. Spek. *J. Appl. Cryst.*, **36**, 7 (2003).

[29] O. Pouralimardan, A.-C. Chamayou, C. Janiak, H. Hosseini-Monfared. *Inorg. Chim. Acta*, **360**, 1599 (2007).
[30] G. Kolawole, K.S. Patel. *J. Chem. Soc., Dalton Trans.*, 1241 (1981).
[31] S.S. Massoud, F.R. Louka, M. Mikuriya, H. Ishida, F.A. Mautner. *Inorg. Chem. Commun.*, **12**, 420 (2009).
[32] Y.-F. Yue, E.-Q. Gao, C.-J. Fang, S. Xu, C.-H. Yan. *J. Mol. Struct.*, **841**, 67 (2007).
[33] X. Zhang, L.-Y. Zhang, L.-X. Shi, Z.-N. Chen. *Inorg. Chem. Commun.*, **12**, 758 (2009).
[34] H. Hosseini-Monfared, S. Alavi, R. Bikas, M. Vahedpour, P. Mayer. *Polyhedron*, **29**, 3355 (2010).