Tris(N,N'-dimethylurea)bis(nitrato-O,O')manganese(II), the first example of a seven-coordinate manganese(II) complex with a monodentate organic ligand

Robby Keuleers [a], Giannis S. Papaefstathiou [b], Catherine P. Raptopoulou [c], Vassilis Tangoulis [c], Herman O. Desseyn [a,*], Spyros P. Perlepes [b,*]

[a] *Department of Chemistry, University of Antwerp, RUCA, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[b] *Department of Chemistry, University of Patras, 265 00 Patras, Greece*
[c] *Institute of Materials Science, NCSR 'Demokritos', 153 10 Aghia Paraskevi Attikis, Greece*

Abstract

Employing a variety of solvents and molar ratios, the reactions of $Mn(NO_3)_2 \cdot 6H_2O$ with N,N'-dimethylurea (DMU) afforded the adduct $[Mn(NO_3)_2(DMU)_3]$ (**1**). X-ray analysis shows that the high-spin complex has a pentagonal bipyramidal geometry with two DMU oxygen atoms in axial positions and with two types of monodentate O-bonding for the DMU molecules, one of them being very unusual. The spectroscopic properties of the prepared complex are also discussed.   © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Manganese(II) complexes; Nitrate complexes; N,N'-Dimethylurea complexes; Pentagonal bipyramidal geometry; EPR

1. Introduction

High-spin manganese(II) complexes are characterized by the absence of ligand field stabilization energy, and this has two main consequences: (i) the possibility to obtain various coordination geometries, and (ii) a lower stability of manganese(II) complexes compared with those of other divalent 3d metals. With regard to the first point, coordination numbers exceeding six are, however, not common for manganese(II) [1]. Polydentate chelating ligands or rigid, resonance-stabilized planar organic ligands have been employed to enforce higher coordination numbers [2].

We have recently become interested in the development of the coordination chemistry of urea and its derivatives in an attempt to create novel supramolecular structures. We report here the first example, to our knowledge, of a high-spin seven-coordinate manganese(II) complex where the metal ion is coordinated by a monodentate organic ligand.

2. Experimental

All manipulations were performed under aerobic conditions. $Mn(NO_3)_2 \cdot 6H_2O$ and N,N'-dimethylurea (DMU) were used as received (Aldrich). All solvents were of reagent grade obtained from commercial sources and used without further purification.

2.1. Instrumentation

C, H and N analyses were conducted by the University of Ioannina, Greece, Microanalytical Service. IR spectra (4000–$500 \, cm^{-1}$) were recorded on a Perkin-Elmer 16 PC spectrometer as KBr pellets, and on a Bruker IFS 113v Fourier-transform (FT) spectrometer with samples prepared as Nujol or perfluorocarbon mulls between KBr plates. Far-IR spectra (500–$50 \, cm^{-1}$) were recorded on a Bruker IFS 113v FT spectrometer with a DTGS detector using polyethylene pellets. FT Raman data have been collected on a Bruker IFS 66v spectrometer equipped with a FRA 106 Raman accessory, a CW Nd:YAG laser source and a liquid nitrogen-cooled Ge detector. The solid-state EPR spectrum at 4 K was recorded on a Bruker ER 200D-SC X-band spectrometer, equipped with an Oxford ESR 9 cryostat. The magnetic sus-

* Corresponding authors. H.O. Desseyn: Tel.: +32-32-180365; Fax: +32-32-180233; E-mail: Keuleers@ruca.ua.ac.be. S.P. Perlepes: Tel.: +30-61-997146; Fax: +30-61-997118; E-mail: perlepes@patreas.upatras.gr

ceptibility was measured at room temperature by the Faraday method with a Cahn-Ventron RM-2 balance standardized with $HgCo(NCS)_4$. The molar susceptibility was corrected for the diamagnetism of the constituent atoms using Pascal's constants.

2.2. Preparation of [Mn(NO₃)₂(DMU)₃] (1)

A solution of $Mn(NO_3)_2 \cdot 6H_2O$ (0.29 g, 1.0 mmol) in Me_2CO (10 ml) was added to a solution of DMU (0.31 g, 3.5 mmol) in the same solvent (8 ml). To the colourless solution obtained, Et_2O (25 ml) was added and, soon, a white microcrystalline solid began to appear. The reaction mixture was stirred for 5–10 min at room temperature. The precipitate was collected by filtration, washed with Et_2O and dried in vacuo over P_4O_{10}. Yield: 0.40 g (75%). Crystals suitable for X-ray structural analysis were obtained by slow evaporation of the initial reaction solution in Me_2CO at 15°C. Employment of higher DMU:Mn^{II} molar ratios (5:1, 7:1) gave again complex **1**. The same product can also be isolated by using DMU:Mn^{II} ratios of 2:1, 4:1 and 7:1 in EtOH or MeCN. *Anal.* Calc. for $C_9H_{24}N_8MnO_9$: C, 24.56; H, 5.46; N, 25.28. Found: C, 24.61; H, 5.55; N, 25.54%. Selected IR and far-IR data (cm^{-1}): 3367 vs $[\nu(NH)]$, 1650 m $[\nu_1(A_1)NO_3^-]$, 1639 vs and 1610 sh $[\nu_{as}(CN) + \delta_{as}(NH)]$, 1621 vs and 1585 m $[\nu(CO)]$, 1514 m $[\delta_s(NH)]$, 1312 m $[\delta_{as}(NH) + \nu_{as}(CN)]$, 1288 sh $[\nu_5(B_2)NO_3^-]$, 1194 m and 1172 m $[\nu_s(N-CH_3)]$, 1049 w $[\nu_2(A_1)NO_3^-]$, 1038 sh and 1029 m $[\nu_{as}(N-CH_3)]$, 928 vw and 893 vw $[\nu_s(CN)]$, 777 w and 756 w $[\pi(CO)]$, 735 sh $[\nu_3(A_1)NO_3^-]$, 704 sh and 645 sh $[\delta(CO)]$, 614 m and 515 w $[\delta(NCN)]$, 576 mb $[\pi_{as}(NH)]$, 346 mb and 280 sh $[\nu(Mn-O_{DMU})]$, 299 sb, 221 sh and 195 sb $[\nu(Mn-O NO_3^-)]$. Selected Raman data (cm^{-1}): 1645 w and 1610 w $[\nu_{as}(CN) + \delta_{as}(NH)]$, 1621 w and 1585 w $[\nu(CO)]$, 1037 vs $[\nu_{as}(N-CH_3)]$, 936 m and 894 m $[\nu_s(CN)]$.

2.3. X-ray crystallography

A brief summary of the crystal data, data collection and structure solution and refinement parameters for complex **1** is given in Table 1. A colourless prismatic crystal with approximate dimensions $0.10 \times 0.20 \times 0.50$ mm was mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range $11 < 2\theta < 23°$. Intensity data were recorded using a θ–2θ scan to $2\theta_{max} = 50°$. Lorentz, polarization and Ψ-scan absorptions were applied. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on F^2 with SHELXL-93. All hydrogen atoms were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically.

Table 1
Crystallographic data for complex **1**

Chemical formula	$C_9H_{24}N_8MnO_9$
Formula weight	443.30
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	17.665(8)
b (Å)	8.819(4)
c (Å)	13.509(7)
β (°)	112.34(1)
V (Å^3)	1946.5(2)
Z	4
T (K)	298
D_{calc} (Mg m^{-3})	1.513
μ (mm^{-1})	0.737
Reflections collected	3596
Independent reflections	3440 ($R_{int} = 0.0507$)
Observed $(I > 2\sigma(I))$ reflections	2938
Parameters refined	340
Largest residuals (e Å^{-3})	0.521, −0.743
$R1$ on F (observed data)	0.0572
$wR2$ on F^2 (observed data)	0.1634
GOF on F^2	1.090

3. Results and discussion

The crystal structure of complex **1** consists of $[Mn(NO_3)_2(DMU)_3]$ molecules (Fig. 1) joined together by hydrogen bonds. The Mn^{II} atom is surrounded by three O-bonded DMU ligands and two bidentate chelating nitrate groups. The nitrato ligands are planar, the sum of the three O–N–O angles being 360°. Both are classified as 'bidentate', not 'anisobidentate', nitrates using the criteria of Reedijk and co-workers [3].

Complex **1** extends to four the number of structurally characterized complexes of DMU. The other three complexes are $[MnBr_2(DMU)_3]$ (**2**) [4], $[Fe(DMU)_6](ClO_4)_3$ [5] and $[Er(DMU)_6(H_2O)](ClO_4)_3$ [6].

The coordination polyhedron is a distorted pentagonal bipyramid, with the DMU oxygens O(1) and O(11) occupying the axial positions (O(1)–Mn–O(11) 171.3(1)°). Four out of five equatorial angles deviate significantly from the ideal value of the pbp geometry (72°); this is due to the restricted 'bite' of the chelating nitrato groups with angles at the metal of 54.1 and 53.7°. Thus, the geometry about Mn is significantly distorted, and the five atoms O(21), O(31), O(32), O(41) and O(42) defining the equatorial plane deviate from that plane by an average of 0.127 Å (maximum deviation by O(41), 0.165 Å); Mn lies 0.056 Å out of the least-squares equatorial plane towards O(1). The present compound joins a small family of seven-coordinate manganese(II) complexes [1,2,7–13], being the first one in which the organic ligands (the DMU molecules) are monodentate. It is interesting to note that the coordination geometry of the metal is not forced by the geometrical demands of the organic ligand like in almost all reported seven-coordinate manganese(II) species.
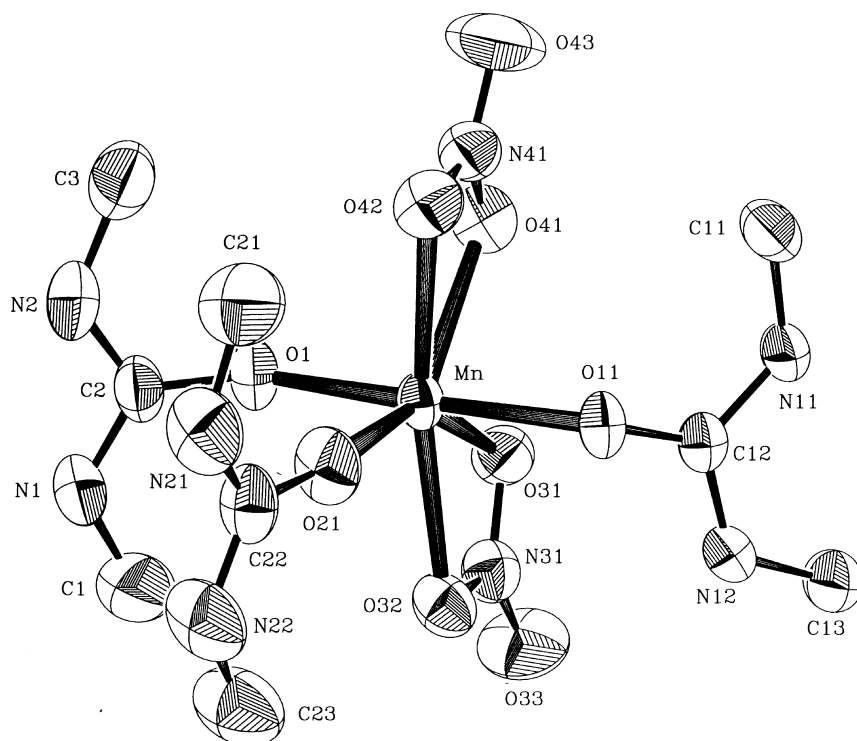
Fig. 1. An ORTEP representation of complex **1**. Selected bond lengths (Å) and angles (°): Mn–O(1) 2.136(3), Mn–O(11) 2.155(2), Mn–O(21) 2.090(3), Mn–O(31) 2.368(3), Mn–O(32) 2.384(3), Mn–O(41) 2.326(3), Mn–O(42) 2.379(3), O(1)–Mn–O(11) 171.3(1), O(1)–Mn–O(21) 94.1(1), O(31)–Mn–O(32) 53.7(1), O(32)–Mn–O(21) 91.9(1), O(21)–Mn–O(42) 87.9(1), O(42)–Mn–O(41) 54.1(1), O(41)–Mn–O(31) 73.3(1), O(11)–Mn–O(42) 85.1(1).

The axial Mn–O distances (2.136(3) and 2.155(2) Å) are normal [4] for a bent coordinated DMU molecule (Mn–O(1)–C(2) 135.5(2)°, Mn–O(11)–C(12) 127.8(2)°), each oxygen atom sharing one lone pair with the metal ion. This is the usual way of coordination of urea and its derivatives [14]. The equatorial Mn–O(21) bond length of 2.090(3) Å (with a Mn–O(21)–C(22) angle of 164.6(3)°) is shorter than the axial ones. Linearly or approximately linearly coordinated urea or urea derivatives are extremely unusual and have been observed only in a few cases [4,14]. This rare behaviour has been discussed by Delaunay and Hugel for complex **2** in terms of electronic structure and π-acceptor capacity of the planar DMU ligand [4].

The crystal structure is stabilized through a complex scheme of intermolecular hydrogen bonds creating a 3D network and involving all six DMU nitrogens, the two axial DMU oxygens and some (O(31), O(33), O(41)) nitrate oxygens; the strongest hydrogen bond appears to be N(11)–H···O(11) [0.5 − x, −0.5 + y, −0.5 − z], its dimensions being N(11)···O(11) 2.91, H···O(11) 2.16 Å and N(11)–H···O(11) 155°. There is also one weak intramolecular hydrogen bond between the N(12) proton and atom O(32). The non-participation of the equatorial DMU oxygen atom (O(21)) in hydrogen bonding may be explained by the lower electron density on this oxygen, compared to the axial oxygens, due to the smaller degree of electron delocalization, as can be seen from the C=O bond distances (C=O$_{eq}$ = 1.240(5) Å, C=O$_{axial}$ = 1.264(4) and 1.269(4) Å).

The appearance of two bands for each DMU mode in the IR spectrum of **1** (see Section 2) is due to the presence of two different DMU ligands. For example, the $\nu(CO)$ and $\nu_{as}(CN) + \delta_{as}(NH)$ vibrations of free DMU appear at 1628 and 1591 cm^{-1}, respectively. In the spectrum of **1**, the two bands at 1621 and 1585 cm^{-1} are assigned to $\nu(CO)$, while the bands at 1639 and 1610 cm^{-1} are attributed to $\nu_{as}(CN) + \delta_{as}(NH)$. The bands that exhibit the smaller shift (1621 and 1610 cm^{-1}) are due to the linearly bonded DMU molecule, because this type of coordination implies a smaller degree of electron delocalization within the > NCON < moiety compared to the lone pair-bonded DMU molecules, in full agreement with the X-ray analysis. The nitrate vibrations are indicative of the presence of bidentate chelating nitrato groups, because [15,16] the separation of the two highest frequency bands $\nu_1(A_1)$ and $\nu_5(B_2)$ (under C_{2v} symmetry) is large.

The room-temperature effective magnetic moment has been measured for **1**. As might be expected, the complex shows a typical high-spin d^5 behaviour with a μ_{eff} value of 5.87 BM [17].

The X-band EPR spectrum of a powdered sample of complex **1** at 4 K is shown in Fig. 2. The spectrum consists of a broad line centred at $g \sim 2.0$ flanked by several features at lower and higher fields. Such spectra are common for weakly coupled manganese(II) complexes and correspond to the superimposition of spectra of the various excited spin states of the Mn^{II} pairs, modulated by a Boltzmann distribution
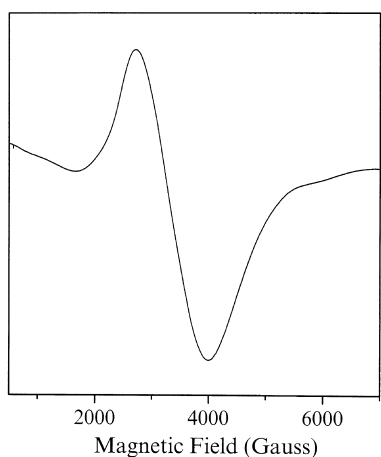
Fig. 2. X-band EPR spectrum of a powdered sample of **1** at 4 K.

[18]. Contributions from the first and second excited states can be clearly identified in the spectrum.

Undoubtedly, the chelating/macrocyclic nature of the organic ligands and/or the resonance-stabilized planarity of the systems are important factors in imposing pentagonal bipyramidal geometry [19]. However, the structure of **1** discussed above suggests that, in the particular case of a d^5 ion with no stereochemical preferences, the structural requirements leading to seven coordination are less stringent. In our complex, the higher than six coordination number is due to the small chelate bite angle of the nitrato ligands, which renders four-membered chelate rings with the metal ion and leaves ample space for three more monodentate donors in the coordination sphere [20]. Work in progress demonstrates the ability of the DMU/NO_3^- ligand combinations to give high coordination numbers and a variety of geometries for 3d metal ions.

4. Supplementary material

Full crystallographic data, positional and equivalent thermal parameters of the non-H atoms, anisotropic thermal parameters of the non-H atoms, positional and isotropic thermal parameters of the H atoms, lists of bond lengths and angles and details of the H bonds are available from the authors on request.

Acknowledgements

References

[1] M. Mikuriya, Y. Hatano, E. Asato, Bull. Chem. Soc. Jpn. 70 (1997) 2945 and Refs. therein.
[2] B. Chiswell, E.D. McKenzie, L.F. Lindoy, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 4, Pergamon, Oxford, 1987, Ch. 41, pp. 1–122.
[3] G.J. Kleywegt, W.G.R. Wiesmeijer, G. van Driel, W.L. Driessen, J. Reedijk, J.H. Noordik, J. Chem. Soc., Dalton Trans. (1985) 2127.
[4] J. Delaunay, R.P. Hugel, Inorg. Chem. 25 (1986) 3957.
[5] G. Galeazzi, U. Russo, G. Valle, S. Calogero, Trans. Met. Chem. 6 (1981) 325.
[6] M.C. Mattos, E. Surcouf, J.-P. Mornon, Acta Crystallogr., Sect. B 33 (1977) 1855.
[7] Z. Sun, P.K. Gantzel, D.N. Hendrickson, Polyhedron 17 (1998) 1511.
[8] X.S. Tan, D.F. Xiang, W.X. Tang, J. Sun, Polyhedron 16 (1997) 689.
[9] M.S. Lah, H. Chun, Inorg. Chem. 36 (1997) 1782.
[10] S. Gou, X. You, K. Yu, J. Lu, Inorg. Chem. 32 (1993) 1883.
[11] S. Brooker, V. McKee, Acta Crystallogr., Sect. C 49 (1993) 441 and Refs. therein.
[12] A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, V. Marcelino, M. Micheloni, P. Paoletti, P. Paoli, Inorg. Chem. 29 (1990) 1716.
[13] C. Pelizzi, G. Pelizzi, P. Tarasconi, J. Chem. Soc., Dalton Trans. (1985) 215.
[14] L. Lebioda, Acta Crystallogr., Sect. B 36 (1980) 271.
[15] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986, pp. 254–257.
[16] U. Casellato, P.A. Vigato, M. Vidali, Coord. Chem. Rev. 36 (1981) 183.
[17] R.L. Carlin, Magnetochemistry, Springer, Berlin, 1986, p. 53.
[18] S.V. Khangulov, V.V. Barynin, N.V. Voevodskaya, A.I. Grebenko, Biochim. Biophys. Acta 1020 (1990) 305.
[19] S. Brooker, V. Mckee, J. Chem. Soc., Dalton Trans. (1990) 2397.
[20] J. Drummond, J.S. Wood, J. Chem. Soc. A (1970) 226.