

N,N'-diethyl and N-ethyl,N'-methyl glyoxal-bridged cyclams: synthesis, characterization, and bleaching activities of the corresponding Mn(II) complexes

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Abstract The synthesis and characterization of N,N'-diethyl (L-Et,Et) and N-ethyl,N'-methyl (L-Et,Me) glyoxalbridged cyclam ligands are described, together with the X-ray crystal structure of the complex [MnCl₂(L-Et,Me)]. Bleaching of morine in the presence of hydrogen peroxide by the corresponding Mn catalysts [MnCl₂(L-Et,Et)], [MnCl₂(L-Et,Me)] and [MnCl₂(L-Me,Me)] has been studied in aqueous solution at three different pH values (8.0, 8.75, and 9.0). The results clearly show that increasing pH has a different effect on the three catalysts, and that the dimethyl derivative is by far the most active.

Introduction

Glyoxal-bridged *cyclam*-based ligands (L-R,R') have attracted much interest [1–9] in the last decades, due to their ability to coordinate mid–late transition metals (Scheme 1).

These macrocycles can be easily *N*-functionalized with various groups, allowing the preparation of a wide range of ligands suitable for important applications such as for

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catalysis [4, 8], and the development of metal-based imaging and therapeutic agents in medicine [10].

In particular, manganese(II) complexes of formula $[MnCl_2(\mathbf{L-R,R'})]$ show well-proven peroxide-based bleaching activity, which has been the object of extensive studies documented in the patent literature [11-17]. These complexes were initially targeted as potential oxidation catalysts because the rigid cross-bridged ligand strongly binds the manganese ion and prevents it from being deactivated in the form of MnO_2 . Additional distinctive properties are the presence of the alkyl groups *R* and *R'*, which preclude dimerization and consequent deactivation of the catalyst, and the all-tertiary nature of the nitrogen atoms, which minimizes the possibility of ligand oxidation and catalyst destruction.

Both $[MnCl_2(L-Me,Me)]$ and $[MnCl_2(L-Et,Et)]$ are patented bleach catalysts, which have been heavily investigated by the laundry detergent industry because of their ability to activate O2/H2O2 in water and remove stain molecules from cloth. The crystal structures of both complexes [5, 18] have been recently reported, demonstrating also the academic interest [19, 20] toward this class of compounds. Despite this attention, the detailed synthesis of L-Et,Et has never been reported in the literature, as well as the preparation of the mixed L-Et,Me species, which has also been mentioned in the patent literature. Aiming to fill this gap, this paper presents the synthesis of L-Et,Et and L-Et,Me (Scheme 1) along with their NMR characterization. In addition, the preparation of the corresponding MnCl₂ complexes, which have been tested in the bleaching of morine with hydrogen peroxide, in comparison with [MnCl₂(L-Me,Me)], and the crystal structure of [MnCl₂(L-Et,Me)] are reported.

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Scheme 1 Synthesis of the glyoxal-bridged cyclams L-Et,Me and L-Et,Et: (*i*) glyoxal, MeCN, 50 °C, 5 h; (*ii*) EtI, MeCN, 55 °C, 5d; (*iii*) MeI, MeCN, RT, 3d; (*iv*) NaBH₄, EtOH, RT, 3d; (*v*) NaBH₄, EtOH, RT, 3d

Experimental

Materials and methods

All solvents and reagents were purchased from Sigma-Aldrich and used without further purification. NMR spectra were recorded in D₂O (internal standards: HDO, δ 4.80, for proton spectra, and dioxane, δ 67.0, for carbon spectra) or CD₃CN (internal standards: CD₂HCN, δ 1.96, for proton spectra, and ¹³CD₃CN, δ 1.39, for carbon spectra), using a Bruker 400 DRX spectrometer. UV visible spectra were recorded with a JASCO spectrophotometer. The following abbreviations are used for describing NMR multiplicities: s, singlet; dd, double doublet; ddd, double doublet doublet; dq, double quartet; t, triplet; dt, double triplet; td, triple doublet; m, multiplet. Precursor **1** was prepared according to a described procedure [21].

Synthesis of 3-Et,Et

Ethyl iodide (291 g, 1.86 mol) was added to a solution of **1** (13.8 g, 0.0621 mol) in acetonitrile (450 mL), and the mixture was stirred for 5 days at 55 °C to give a pale yellow crystalline solid. After cooling to room temperature, the product (**3-Et,Et**) was filtered off, washed with

acetonitrile (4 \times 25 mL) and diethyl ether (3 \times 50 mL), and dried under vacuum (yield 15.7 g, 47%).

3-Et,Et

Calcd. (%) for C₁₆H₃₂N₄I₂: C, 35.97, H, 6.04, N, 10.49; found (%): C, 35.78, H, 6.12, N, 10.34. ¹H NMR (400 MHz, D₂O) δ 4.74 (s, 2H, H₆), 4.45 (dt, J = 13.2, 4.4 Hz, 2H, H⁴₄), 3.97 (dq, J = 14.5, 7.2 Hz, 2H, CHHMe), 3.84 (dd, J = 13.0, 4.5 Hz, 2H, H^e₃), 3.64 (dq, J = 14.5, 7.2 Hz, 2H, CHHMe), 3.55 (dt, J = 13.3, 3.9 Hz, 2H, H^a₃), 3.36–3.24 (m, 4H, H^e₄ and H^e₅), 3.24–3.15 (m, 2H, H^e₁), 3.12 (dt, J = 14.1, 3.7 Hz, 2H, H^a₅), 2.74 (td, J = 12.6, 3.4 Hz, 2H, H^a₁), 2.48–2.27 (m, 2H, H^a₂), 2.03–1.88 (m, 2H, H^e₂), 1.46 (t, J = 7.2 Hz, 6H, Me). ¹³C NMR (100 MHz, D₂O) δ 76.5, 60.3, 55.4, 51.5, 46.6 (x2), 18.4, 6.7. The atom labelling is shown in Scheme 2.

Synthesis of 3-Et,Me

Ethyl iodide (291 g, 1.86 mol) was added to a solution of **1** (13.8 g, 0.0621 mol) in acetonitrile (450 mL), and the mixture was stirred for 5 days at 55 °C. After cooling to room temperature, the suspension was filtered, and methyl iodide (27.0 g, 0.190 mol) was added to the filtrate, which was stirred for 3 days at room temperature. The resulting



Scheme 2 Atom labelling for 3-Et,Et, 3-Et,Me, L-Et,Me, and L-Et,Et

white solid (**3-Et,Me**) was collected by filtration, washed with acetonitrile $(3 \times 20 \text{ mL})$ and diethyl ether $(3 \times 20 \text{ mL})$, and dried under vacuum (yield 13.2 g, 41%).

3-Et,Me

Calcd. (%) for C₁₅H₃₀N₄I₂: C, 34.63, H, 5.81, N, 10.77; found (%): C, 34.33, H, 5.89, N, 10.60. ¹H NMR (400 MHz, D₂O) δ 4.80 (s, 1H, H₆), 4.74 (s, 1H, H₆), 4.58 (dt, *J* = 12.8, 4.0 Hz, 1H, H^a₄), 4.51 (dt, *J* = 12.8, 3.6 Hz, 1H, H^a₄), 3.95 (dq, *J* = 14.2, 7.1 Hz, 1H, *CH*HMe), 3.89–3.78 (m, 2H, H^e₃), 3.70 (dt, *J* = 13.6, 3.8 Hz, 1H, H^a₃), 3.69 (dq, *J* = 14.2, 7.1 Hz, 1H, CHHMe), 3.60 (dt, *J* = 13.6, 4.0 Hz, 1H, H^a₃), 3.41 (s, 3H, Me), 3.38–3.10 (m, 8H, H^e₁, H^e₄, H^s₅ and H^e₅), 2.79 (ddd, *J* = 12.5, 7.8, 3.0 Hz, 2H, H^a₁), 2.51–2.31 (m, 2H, H^a₂), 2.03–1.90 (m, 2H, H^e₂), 1.46 (t, *J* = 7.1 Hz, 3H, Me). ¹³C NMR (100 MHz, D₂O) δ 77.1, 76.4, 65.6, 60.3, 55.7, 51.6 (×2), 50.0, 48.6, 47.1, 46.8, 46.5, 18.9, 18.5, 6.8. The atom labelling is shown in Scheme 2.

Synthesis of L-Et, Et and L-Et, Me

To a suspension of **3-Et,Et** (6.8 g, 0.0127 mol) or **3-Et,Me** (6.6 g, 0.0127 mol) in ethanol (200 mL) was slowly added NaBH₄ (4.82 g, 0.127 mol). The reaction mixture was stirred at room temperature for 3 days. Excess NaBH₄ was decomposed by the addition of concentrated HCl until pH <2. Absolute ethanol (400 mL) was then added to the mixture and the solvents were removed under vacuum, giving a white solid. This was dissolved in KOH 8 M (75 mL), and the water phase was extracted with toluene (5 × 150 mL). The combined organic phases were dried over sodium sulfate, and the solvent was removed under vacuum to afford the product as a yellow oil (yield 60–70%).

L-Et,Et

Calcd. (%) for C₁₆H₃₄N₄: C, 68.03, H, 12.13, N, 19.83; found (%): C, 67.86, H, 12.19, N, 19.78. ¹H NMR (400 MHz, CD₃CN) δ 3.66 (td, J = 11.8, 4.5 Hz, 2H, H₃), 3.21 (AA' of AA'XX', J = 8.8 Hz, 2H, H₆), 2.76 (td, J = 11.8, 4.0 Hz, 2H, H₁), 2.65 (m, 2H), 2.57 (dq, J = 12.4, 7.2 Hz, 2H, CH*H*Me), 2.51 (AA' of AA'XX', J = 8.8 Hz, 2H, H₆'), 2.52–2.38 (m, 6H), 2.34 (m, 2H, H_{3'}), 2.30 (m, 2H, H_{1'}), 2.16 (dq, J = 12.4, 6.8 Hz, 2H, CH*H*Me), 1.58–1.41 (m, 2H, H₂), 1.41–1.09 (m, 2H, H_{2'}), 1.00 (t, 6H, Me). ¹³C NMR (100 MHz, CD₃CN) δ 59.2, 58.8, 57.9, 55.0, 52.1, 49.0, 29.0, 13.8. The atom labelling is shown in Scheme 2.

L-Et,Me

Calcd. (%) for C₁₅H₃₂N₄: C, 67.11, H, 12.02, N, 20.87; found (%): C, 67.35, H, 12.21, N, 20.63. ¹H NMR (400 MHz, CD₃CN) δ 3.79 (td, J = 11.5, 4.6 Hz, 1H, H₃), 3.62 (td, J = 11.5, 4.6 Hz, 1H, H₃), 3.25–3.18 (m, 1H, H₆), 3.13–3.06 (m, 1H, H₆), 2.76 (td, J = 12.8, 4.0 Hz, 1H, H₁), 2.73–2.29 (m, 16H, H₁, H_{1'} × 2, H_{3'} × 2, H₄ × 2, H_{4'} × 2, H₅ × 2, H_{5'} × 2, H_{6'} × 2, CHHMe), 2.16 (s, 3H, Me), 2.15 (m, 1H, CH*H*Me), 1.55–1.44 (m, 2H, H₂), 1.42– 1.32 (m, 2H, H_{2'}), 1.0 (t, 3H, Me). ¹³C NMR (100 MHz, CD₃CN) δ 61.7, 59.2, 58.8, 57.9, 57.7, 57.0, 56.8, 55.0, 52.2 (×2), 49.1, 43.0, 29.0, 28.7, 13.8. The atom labelling is shown in Scheme 2.

Synthesis of [MnCl₂(L-Et,Et)] [15] and [MnCl₂(L-Et,Me)]

Anhydrous $MnCl_2$ (0.97 g, 0.0077 mol) was dissolved in dry dimethylacetamide (12 mL) under nitrogen at 100 °C with stirring. To the solution was added the appropriate

ligand (0.0077 mol), and the reaction mixture was stirred at 100 °C for 3 h. The system was cooled, and the white microcrystalline solid was filtered off and washed with dimethylacetamide (2 × 10 mL), diethyl ether (5 × 10 mL), and dried under vacuum (yield 80–90%). [MnCl₂(**L-Et,Me**)]: calcd. (%) for $C_{15}H_{32}Cl_2MnN_4$: C, 45.69, H, 8.18, N, 14.21; found (%): C, 45.94, H, 8.28, N, 14.02.

Bleaching tests

Preparation of the solutions: Buffer solutions (**A**) at constant ionic strength (1 M NaCl) were prepared by dissolving NaCl (58.4 g, 1.0 mol) and NaHCO₃ (8.4 g, 0.10 moL) in water (1.0 L). The pH was then adjusted to the desired value by the addition of Na₂CO₃. A solution (**B**) of morin (7.5 mM) was prepared by dissolving morin hydrate (0.018 g, 0.060×10^{-3} mol) in ethanol (8 mL). Solutions (**C**) of the catalysts (0.12 mM) were prepared by dissolving the complexes in the buffered solutions (**A**, 50 mL).

Catalytic runs: An aliquot of the catalyst solution C (500 μ L) was diluted in the appropriate buffer solution A (25 mL), and an aliquot of the morin solution (500 μ L) was added with stirring. The volume was then adjusted to 30 mL by the addition of buffer solution A. An aqueous solution of H_2O_2 (25 µL, 60% w/w) was then added. The concentrations were as initial follows: [cata- $[\text{lyst}] = 2 \times 10^{-3} \text{ mM}, \text{ [morine]} = 0.125 \text{ mM}, \text{ [H}_2\text{O}_2\text{]}$ 0.05% w/w. Progress of the reaction was monitored by following the reduction in the absorption at 396 nm $(\varepsilon = 1.94 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}).$

X-ray structure of [MnCl₂(L-Et,Me)]

Colorless block-shaped single crystals of [MnCl₂(L-Et,Me)], suitable for X-ray analysis, were obtained by slow evaporation of a CH₃CN solution at ambient temperature. X-ray data collection was performed on a Bruker-Nonius Kappa-CCD diffractometer equipped with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data were collected at 173 K under N₂ flow using a Cryostream-700 (Oxford Cryosystems). Unit cell parameters were determined by least-squares refinement of the θ angles of 80 reflections in the range $3.084^{\circ} < \theta < 21.890^{\circ}$. Data reduction and semiempirical absorption corrections were done using EvalCCD [22] and SADABS programs [23], respectively. The structure was solved by direct methods (SIR97 program) [24] and refined by the full-matrix leastsquares methods on F^2 using the SHELXL-97 program [25] with the aid of the program WinGX [26]. All nonhydrogen atoms were refined anisotropically. All H atoms were stereochemically generated and refined by the riding model with $U_{\rm iso} = 1.2 \times U_{\rm eq}$ of the carrier atom $(1.5 \times U_{eq}$ for H atoms of methyl groups). Different Fourier maps showed disorder of the methyl and ethyl groups of the ligand that, owing to the synthetic route, can be attached at N4/N2 or at N2/N4 (refined occupancy factors 0.77 and 0.23, respectively). Thermal ellipsoid plots were generated using Ortep-3 [27] integrated in the WINGX suite of programs. Analysis of structures superimposition was performed using the program Mercury [28]. Crystal and refinement data for [MnCl₂(**L-Et,Me**)] are given in Table 1. CCDC 1483874 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Results and discussion

Synthesis of the macrocycles

The synthesis of macrocycles L-Et,Et and L-Et,Me is outlined in Scheme 1. The bridged precursor 1 was

Table 1 Crystal data and structure refinement parameters for $[MnCl_2(L-Et,Me)]$

Empirical formula	$C_{15}H_{32}Cl_2MnN_4$
Formula weight	394.29
Temperature	173(2) K
Radiation	ΜοΚα
Wavelength	0.71073 Å
Crystal size	0.18 \times 0.13 \times 0.05 mm
Crystal system	Monoclinic
Space group	$P2_{1}/c$
Unit cell dimensions	a = 8.435(3) Å
	b = 13.768(2) Å
	c = 15.587(3) Å
	$\beta = 93.010(18)^{\circ}$
Volume	1807.7(8) Å ³
Ζ	4
Calculated density	1.449 Mg m^{-3}
Absorption coefficient	1.028 mm^{-1}
$\theta_{\max}\theta_{\min}$	27.50°, 3.01°
Limiting indices	$-10 \le h \le 10$
	$-17 \leq k \leq 17$
	$-20 \le l \le 20$
Refins collected/unique	16,114/4069 [R(int) = 0.0753]
Data/restraints/parameters	4069/0/211
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0498, wR2 = 0.0951
R indices (all data)	R1 = 0.0994, wR2 = 0.1160
Max peak/hole (e Å ⁻³)	0.739/-0.406

prepared by reaction of commercial cyclam with glyoxal (step i) as reported in the literature [19].

The iodide salts of type **3** were obtained by sequential alkylation of **1** with the appropriate alkyl iodides (step ii). This reaction is fairly regioselective due to the availability of the lone pairs on the two homotopic exo nitrogens [3]. On the other hand, the two endo nitrogens have lone pairs which are more sterically concealed on the concave face of the cleft-like structure [3], and hence less prone to function as bases.

The ¹H, ¹³C, and 2D COSY NMR spectra of the isolated product were fully consistent with the C_2 symmetry of the molecule, and a unique signal was observed for the couples of homotopic protons related by the axis. As an example, Fig. 1a shows the signal attributed to the axial H₄ protons (for numbering, see Scheme 2 in "Experimental" section), which appear as double triplets.



Fig. 1 Signals of the axial H₄ protons in the ¹H NMR spectra (in D₂O) of **3-Et,Et** (*a*) and **3-Et,Me** (*b*)



The yellow mother liquor was found to contain a substantial amount of the mono-ethylated compound (**2-Et**), as disclosed by the NMR spectrum of the crude mixture. Excess MeI was therefore added, and a new precipitate could be isolated after 5 days of stirring at RT. This product, corresponding to **3-Et**,**Me**, was again characterized by NMR spectroscopy. In this case (Fig. 1b), the diversity of the substituents on the nitrogen atoms reflects on the lack of symmetry of the molecule, and the two axial H₄ protons are not equivalent (Fig. 1b).

The two iodide salts **3-Et,Et** and **3-Et,Me** were then reduced to the pro-ligands **L** with a large excess of NaBH₄ in ethanol (steps iv and v). The milky white reaction media were treated with HCl, and after the initial work-up, the resulting solid was dissolved in 8 M potassium hydroxide. This treatment was necessary in order to extract the free



Scheme 3 Synthesis of complexes $[MnCl_2(L-Et,Et)]$ (R = Me) and $[MnCl_2(L-Et,Me)]$ (R = H)



Fig. 3 ORTEP view of [MnCl₂(**L-Et,Me**)]. Thermal *ellipsoids* are drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Mn1–N1 2.321(3); Mn1–N2 2.333(3); Mn1–N3 2.325(3); Mn1–N4 2.337(3); Mn1–Cl1 2.4574(11); Mn1–Cl2 2.4517(11); N2–Mn1–N4 157.82(10); N1–Mn1–N3 76.14(11); Cl1–Mn1–Cl2 98.50(5). Only the major part of the disordered alkyl groups is shown for clarity

Fig. 2 Signals of the axial H_3 protons in the ¹H NMR spectra (in CD₃CN) of L-Et,Et (*a*) and L-Et,Me (*b*)

ligands with toluene. These molecules act as proton sponges, so it is necessary to use high concentrations of base to ensure their complete deprotonation [3]. At lower pH, the conjugate acid **L-Et,Et-** H^+ was extracted, as confirmed by the presence of a peak at high frequency in its ¹H NMR spectrum.



Fig. 4 Superimposition of the molecular structure of [MnCl₂(L-Et,Me)] with the literature data for [MnCl₂(L-Me,Me)] [2, 5] (*orange*) and [MnCl₂(L-Et,Et)] [16] (*magenta*). (Color figure online)

Both pro-ligands were characterized by NMR spectroscopy. Also in this case, the number of signals is clearly related to the symmetry of the ligands, as illustrated in Fig. 2 for protons H_3 .

Synthesis and structures of the complexes

The synthesis of the complexes was carried out by mixing the ligands and anhydrous $MnCl_2$ in dry dimethylacetamide under a nitrogen atmosphere (Scheme 3).

Colorless block-shaped single crystals of [MnCl₂(**L-Et**,**Me**)] suitable for X-ray analysis were obtained by slow evaporation of a CH₃CN solution at ambient temperature. The complex crystallizes in the monoclinic $P2_1/c$ space group with one molecule contained in the asymmetric unit. The molecular structure is shown in Fig. 3. All of the bond distances fall in the expected ranges.

In this complex, the ligand is topologically constrained in a rigid conformation. The crystal structure confirms the expected geometry already found in other Mn(II) complexes containing this kind of ligand [2, 5, 6, 18]. The Mn atom is hexa-coordinated and occupies the cavity of the tetradentate ligand, completing its coordination sphere with two chlorine atoms in a pseudo-octahedral geometry. The N atoms of the macrobicyclic ligand occupy two axial and two *cis*-equatorial sites of the distorted octahedron, while



Fig. 5 Activities of each catalyst at different pH (a, MnCl₂(L-Me,Me); b, MnCl₂(L-Et,Me); c, MnCl₂(L-Et,Et))



Fig. 6 Comparison of the activities of the three catalysts at different pH values (a, 8.00; b, 8.75; c, 9.00)

the chlorine atoms occupy the two remaining *cis*-equatorial sites. Owing to the synthetic route and to the different substituents at N2 and N4 of the cyclam ligand, Me-/Et-groups can be attached at N4/N2 or at N2/N4 and a disorder in their positions is found in the structure of the complex. Due to the rigidity of the cyclam ligand, only minor differences in geometric parameters are found with respect to similar Mn(II) complexes [2, 5, 18] (Fig. 4). In particular, the structure of [MnCl₂(L-Et,Me)] is isomorphous with the analogous complex of L-Me,Me [2].

Catalytic activities

The catalytic activities of the three Mn(II) complexes [MnCl₂(**L-Et,Et**)], [MnCl₂(**L-Et,Me**)], and [MnCl₂(**L-Me**, **Me**)] for bleaching of morine were compared in buffered aqueous solutions at pH 8.0, 8.75, and 9.0, using hydrogen peroxide as the oxidant. The flavonol morine was chosen for these experiments, since it is present in fruit and vegetables and is a target in the bleaching of laundry [29]. The concentrations used for the experiments were inspired by those conceivably acting during laundry processes, that is, <1 ppm of catalyst and 500 ppm of oxidant. The substrate(morine)/catalyst ratio was set at 60:1. The progress of the reaction was monitored by following the maximum of absorption at 396 nm ($\varepsilon = 1.94 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).

The activities of the three catalysts all depend on pH, but the trends are not the same. Thus, a clear improvement with increasing alkalinity was observed only for $[MnCl_2(L-Me,Me)]$ (Fig. 5a), while the differences are more subtle for $[MnCl_2(L-Et,Me)]$ and $[MnCl_2(L-Et,Et)]$ (Fig. 5b, c). Overall, the dimethyl complex is the most active, particularly at higher values of pH (Fig. 6). These results can be interpreted in light of previous studies [30], which revealed that mononuclear species are active at low pH values, and dinuclear at higher values. It is plausible that this association is favored only for the unhindered dimethyl derivative, and inhibited for the other more sterically crowded complexes.

Conclusion

This work fills a gap in the literature related to macrocyclic ligands derived from cyclam. We have reported the synthesis and characterization of two glyoxal-bridged ligands, whose Mn(II) complexes have been described extensively in the patent literature for their excellent bleaching activity. The X-ray crystal structure of one complex is also described in comparison with closely related compounds. Furthermore, their bleaching activities have been compared in a benchmark test, revealing that pH has a different effect on the three catalysts, and that the dimethyl derivative is by far the most active.

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