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Template synthesis of Mn(II) complexes of tetraazamacrocycles derived from diaminoalkanes and 3,4-hexanedione or benzil

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Abstract: Template condensation of α-diketones, such as 3,4-hexanedione or benzil, with 1,n-diaminoalkanes (where n = 4, 5, 6, 7, 8, 9, 10 or 12) in the presence of Mn(II) resulted in the formation of complexes of the type [MnL(NO_3)]NO_3 (where L = 16 to 32-membered macrocycle). These complexes have been characterized by elemental analyses, conductances, magnetic measurements, as well as IR and electronic spectra.

Keywords: macrocyclic complexes, manganese complexes, IR spectra, electronic spectra.

INTRODUCTION

The template condensation of benzil with 1,2-diaminoethane or 1,3-diaminopropane in the presence of Co^{2+} or Cu^{2+} has been reported to yield macrocyclic complexes.[1,2] A Mn(II) complex of the macrocycle dibenzo-(e,1)(2,3,9,10)-tetraphenyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, derived from benzil and *m*-phenylenediamine, has been reported.[3] By template condensation of 3,4-hexanedione with diaminoalkanes, macrocyclic complexes of Mg(II) and Zn(II) have been synthesized in our laboratories.[4,5] However, Mn(II) complexes of such large ring macrocycles have not been reported so far. In the present paper Mn(II) complexes of 16 to 32-membered tetraazamacrocycles (I, L^1–L^{16}) are described.

EXPERIMENTAL

Materials

1,4-Diaminobutane (Aldrich), 1,5-diaminopentane (Aldrich), 1,6-diaminohexane (Merck), 1,7-diaminoheptane (Aldrich) and 3,4-hexanedione (Aldrich) were purified by distillation before use. Benzil (Otto Kemi) was recrystallized from hot methanol. 1,8-Diaminooctane (Merck), 1,9-diaminononane

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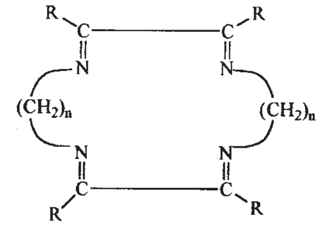


(I)

	R	n
L^1-L^8	C_2H_5	4,5,6,7,8,9,10,12
L^9-L^{16}	C_6H_5	4,5,6,7,8,9,10,12

(Fluka), 1,10-diaminodecane (Fluka) and 1,12-diaminododecane (Aldrich) were used as supplied. $Mn(NO_3)_2.4H_2O$ (Fluka) was of AR grade.

Analytical methods and physical measurements

Manganese was determined volumetrically using EDTA. Nitrogen was determined by the Kjeldahl method. IR spectra were recorded as KBr pellets in the region 400–4000 cm^{-1} on a Nicolet Magna 550 FT IR spectrophotometer. Molar conductances of 10^{-3} M solutions of the complexes were determined in DMSO using a Systronics direct reading conductivity meter 304, cell constant 1.0 cm^{-1}. Magnetic measurements were carried out in the solid state at room temperature on a Gouy balance using $Hg[Co(SCN)_4]$ as the calibrant. Reflectance spectra of the solid compounds, suitably diluted with MgO, were recorded on a Beckman-DU spectrophotometer with a standard Beckman reflectance attachment.

Synthesis of Mn(II) complexes of tetraazamacrocycles derived from 3,4-hexanedione

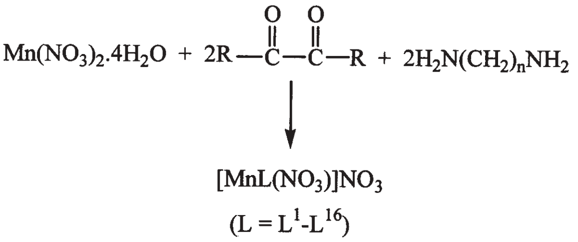
$Mn(NO_3)_2.4H_2O$ (1.0 mmol) was dissolved in ≈ 25 ml of *n*-butanol under stirring and 2.0 mmol of 3,4-hexanedione in ≈ 20 ml of *n*-butanol was added. A solution of diamine (2.0 mmol in ≈ 20 ml of *n*-butanol) was added to this dropwise with constant stirring. A precipitate appeared during the addition and the stirring was continued for 3–4 h. The product was filtered, washed with *n*-butanol and dried *in vacuo*.

Synthesis of Mn(II) complexes of tetraazamacrocycles derived from benzil

$Mn(NO_3)_2.4H_2O$ (1.0 mmol) was dissolved in 25 ml of *n*-butanol under constant stirring. A hot solution of benzil (2.0 mmol in 30 ml of *n*-butanol) was added. To this, a solution of diamine (2.0 mmol in ≈ 20 ml of *n*-butanol) was added dropwise under constant stirring. A precipitate appeared during the addition. The stirring was continued for ≈ 4–5 h and the solid product was filtered, washed with *n*-butanol and dried *in vacuo*.

RESULTS AND DISCUSSION

The reactions of $Mn(NO_3)_2.4H_2O$ with 3,4-hexanedione or benzil with different diaminoalkanes *viz.* 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane, 1,10-diaminodecane or 1,12-diaminododecane in 1:2:2 mole ratios result in the formation of Mn(II) macrocyclic complexes.



$$Mn(NO_3)_2.4H_2O + 2R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R + 2H_2N(CH_2)_nNH_2 \longrightarrow [MnL(NO_3)]NO_3 \quad (L = L^1\text{-}L^{16})$$

The resulting macrocyclic complexes are brown solids, insoluble in water, methanol, acetone, carbon tetrachloride, acetonitrile, nitromethane and chloroform but soluble in dimethyl sulphoxide. The characteristics and analysis of the complexes are given in Table I.

TABLE I. Analyses and physical characteristics of the Mn(II) complexes of the tetraazamacrocycles

Complex	Yield %	Analyses (%); Found (Calcd.)		Molar conductances $\Omega^{-1}cm^2mol^{-1}$
		N	Mn	
$[MnL^1NO_3]NO_3$	54	11.08 (10.95)	10.92 (10.74)	90
$[MnL^2NO_3]NO_3$	36	10.18 (10.38)	10.31 (10.18)	50
$[MnL^3NO_3]NO_3$	46	9.93 (9.87)	9.83 (9.67)	85
$[MnL^4NO_3]NO_3$	43	9.37 (9.40)	9.39 (9.22)	56
$[MnL^5NO_3]NO_3$	47	9.09 (8.98)	8.98 (8.80)	80
$[MnL^6NO_3]NO_3$	68	8.65 (8.59)	8.53 (8.42)	84
$[MnL^7NO_3]NO_3$	37	8.32 (8.24)	8.26 (8.08)	63
$[MnL^8NO_3]NO_3$	46	7.73 (7.61)	7.52 (7.46)	91
$[MnL^9NO_3]NO_3$	43	8.08 (7.96)	7.91 (7.80)	90
$[MnL^{10}NO_3]NO_3$	49	7.71 (7.65)	7.60 (7.50)	50
$[MnL^{11}NO_3]NO_3$	38	7.42 (7.37)	7.27 (7.23)	90
$[MnL^{12}NO_3]NO_3$	42	7.19 (7.11)	7.06 (6.97)	74
$[MnL^{13}NO_3]NO_3$	40	6.66 (6.86)	6.89 (6.73)	85
$[MnL^{14}NO_3]NO_3$	35	6.71 (6.63)	6.56 (6.50)	70
$[MnL^{15}NO_3]NO_3$	40	6.49 (6.42)	6.36 (6.30)	51
$[MnL^{16}NO_3]NO_3$	34	6.11 (6.03)	6.01 (5.91)	80

During the template synthesis of Fe(II), Co(III) and Ni(II) complexes of MePhTIM, Eggleston and Jackels[6] ruled out the possibility of the formation of diazepine, a 1+1 condensation product, on the basis of the ^{1}H-NMR spectra.

For tetraazamacrocycles, the M–N bond lengths for which the strain energy in the macrocycle is minimum have been calculated and ideal ring sizes of metal ions have been investigated.[7,8] The M–N bond lengths for transition metal complexes of 12- to 16-membered saturated tetraazamacrocycles range from 1.8–2.4 Å and hence many macrocycles of varying ring sizes coordinate readily to transition metal ions to give stable complexes.[9] There will be greater flexibility in the larger rings due to which metal ions smaller than the macrocyclic ring size can also be conveniently accommodated resulting in the formation of stable complexes. The formation constants and molecular mechanics calculations have confirmed that the chelate ring size is important in controlling the metal ion size-based selectivity and usually outweighs the macrocyclic ring size in this respect.[10,11]

Infrared spectra

In the IR spectra of Mn(II) complexes of tetraazamacrocycles (Table II), no absorption band was observed at 1700 cm^{-1} and 3200–3400 cm^{-1} indicating the absence of unreacted >C=O or $-NH_2$ groups.[12,13] A strong absorption band in the region 1600–1640 cm^{-1} may be attributed to the coordinated >C=N group.[14,15] Intense absorption bands at 710–740, 810–830 and 1380 cm^{-1} are assigned to ionic nitrate and those at 1000–1030, 1260–1280 and 1500–1520 cm^{-1} to unidentate coordinated nitrate.[16,17]. In the Mn(II) complexes of macrocycles derived from benzil, medium intensity bands in the region 1560–1590 cm^{-1} are attributed to ν(C=C) of phenyl groups and bands at 740–780 cm^{-1} to C–H out of plane bending of phenyl groups.[3]

TABLE II. IR spectral data of the Mn(II) complexes of the tetraazamacrocycles

Complex	IR bands (cm^{-1})			
	ν(C=N)	$-NO_3$ ionic	$-NO_3$ unidentate	ν(C=C)
$[MnL^1NO_3]NO_3$	1600*s*; 1640*s*	720*w*; 830*s*; 1380*s*	1030*s*; 1280*s*; 1520*s*	–
$[MnL^2NO_3]NO_3$	1600*s*; 1630*s*	730*w*; 830*w*; 1380*s*	1010*w*; 1510*s*	–
$[MnL^3NO_3]NO_3$	1600*s*; 1640*s*	730*w*; 830*s*; 1380*s*	1030*m*; 1500*s*	–
$[MnL^4NO_3]NO_3$	1630*s*	730*w*; 830*m*; 1380*s*	1030*wb*; 1520*s*	–
$[MnL^5NO_3]NO_3$	1600*s*; 1630*s*	740*w*; 830*w*; 1380*s*	1000*w*; 1260*w*; 1500*s*	–
$[MnL^6NO_3]NO_3$	1600*s*; 1640*s*	730*m*; 830*w*; 1380*s*	1030*w*	–
$[MnL^7NO_3]NO_3$	1600*s*; 1640*s*	720*w*; 830*w*; 1380*s*	1010*w*; 1510*m*	–
$[MnL^8NO_3]NO_3$	1600*s*; 1640*s*	720*w*; 830*w*; 1380*s*	1000*w*; 1520*s*	–
$[MnL^9NO_3]NO_3$	1600*s*; 1640*s*	720*m*; 830*s*; 1380*s*	1010*s*; 1290*s*; 1520*s*	1560*s*
$[MnL^{10}NO_3]NO_3$	1600*s*;	730*m*; 830*m*; 1380*s*	1010*w*; 1520*s*	1560*s*
$[MnL^{11}NO_3]NO_3$	1600*s*; 1640*s*	720*m*; 830*s*; 1380*s*	1030*m*; 1530*s*	1560*s*
$[MnL^{12}NO_3]NO_3$	1610*s*;	720*m*; 810*s*; 1380*s*	1020*m*; 1270*m*	1570*m*
$[MnL^{13}NO_3]NO_3$	1600*s*; 1640*s*	720*m*; 830*w*; 1380*s*	1010*w*; 1510*s*	1580*s*
$[MnL^{14}NO_3]NO_3$	1610*m*;	720*w*; 810*m*; 1380*m*	1010*m*; 1270*w*; 1510*m*	1560*m*
$[MnL^{15}NO_3]NO_3$	1600*s*	710*w*; 810*w*; 1380*s*	1010*w*; 1260*w*; 1520*m*	1590*m*
$[MnL^{16}NO_3]NO_3$	1600*s*	730*m*; 830*m*; 1380*s*	1000*w*; 1500*s*	1560*s*

Conductances

The molar conductances of 10^{-3} M solutions of the complexes in DMSO fall in the range 50–91 $\Omega^{-1}cm^2mol^{-1}$ indicating that they are 2:1 electrolytes. Thus, in solution both the nitrate groups are ionized whereas in the solid state one of the nitrate groups behaves as unidentate as evidenced by the IR spectra. For Mn(II) complexes of macrocycles derived from 1,10-phenanthroline and 2,6-diacetylpyridine, Lewis *et* *al.*,[18] reported conductances in DMSO in the range 50–80 $\Omega^{-1}cm^2mol^{-1}$, confirming their 2:1 electrolytic behaviour.

TABLE III. Magnetic moments of the Mn(II) complexes of the tetraazamacrocycles

Complex	μ_{eff} (B.M.)
$[MnL^1NO_3]NO_3$	4.95
$[MnL^3NO_3]NO_3$	5.77
$[MnL^5NO_3]NO_3$	6.26
$[MnL^8NO_3]NO_3$	5.96
$[MnL^9NO_3]NO_3$	5.96
$[MnL^{11}NO_3]NO_3$	6.67
$[MnL^{13}NO_3]NO_3$	5.50
$[MnL^{16}NO_3]NO_3$	6.77

Electronic spectra

The diffuse reflectance spectra of the Mn(II) complexes of tetraazamacrocycles derived from diaminoalkanes and 3,4-hexanedione or benzil exhibit bands in the region 13690–14285 cm^{-1} which may be charge transfer bands. Bands in the region 18000–18200 and 24200–25000 cm^{-1} may be assigned to the $^6A_{1g}$ (s) → ^{4} T_{1g} (s) and $^6A_{1g}$ (s) → $^4E_g + {}^4A_{1g}$ (G) multiplicity forbidden transitions, respectively.[19] The electronic spectra are quite similar to those of octahedral Mn(II) complexes. However, the complexes seem to be pentacoordinated as evidenced by IR spectroscopy. Thus, it appears that the anions are coordinated to some extent giving distorted octahedral geometry.

Magnetic moments

The μ_{eff} values of the Mn(II) tetraazamacrocyclic complexes at room temperature (Table III) indicate the presence of high spin Mn(II). Lower magnetic moment values for Mn(II) complexes of macrocycles derived from 3,4-hexanedione may be due to Mn–Mn interaction since these complexes might have a tendency to dimerise.[20] However, for the Mn(II) complexes of macrocycles derived from benzil, the μ_{eff} values are close to the expected values for five unpaired electrons,[3] as these complexes will not dimerise due to the presence of the bulkier phenyl groups. The lower values of the magnetic moments for the former complexes may be due to antiferromagnetism caused by pairing of the moments on adjacent atoms which point in opposite directions.[21] As a result of this, the μ_{eff} values will be lower than expected for an array of independent ions. The lower valeus of the magnetic moments may also arise because of the presence of traces of Mn(III) as a result of aerial oxidation of Mn(II) during synthesis.[22]

In case of Mn(II) complexes of the macrocycles derived from the same α-diketone and different diaminoalkanes, the μ_{eff} values increase with increasing carbon-carbon chain length of the amine residue. This may be due to steric hindrance caused by the folding of the longer carbon-carbon chain which reduces the Mn-Mn interaction thereby increasing the μ_{eff} values.

These macrocyclic complexes are high spin even in the presence of strongly coordinating azomethine groups. This is probably due to the saddle shape of the macrocycle and the sitting atop of the Mn(II) centre with respect to N_4 macrocyclic plane.[23]

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ИЗВОД

ТЕМПЛАТНА СИНТЕЗА КОМПЛЕКСА Mn(II) СА ТЕТРААЗАМАКРОЦИКЛИМА ИЗВЕДЕНИМ ОД ДИАМИНОАЛКАНА И 3,4-ХЕКСАНДИОНА ИЛИ БЕНЗИЛА

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Темплатна синтеза α-дикетона, као што су 3,4-хександион или бензил, са 1,n-диаминоалканима (где је n = 4, 5, 6, 7, 8, 9, 10 или 12) у присуству Mn(II) довела је до стварања комплекса типа $[MnL(NO_3)]NO_3$ (где је L = 16 до 32-члани макроцикл). Ови комплекси карактерисани су елементалном анализом, мерењем проводљивости, магнетним мерењима, као и IR и електронским спектрима.

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