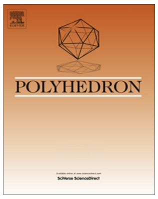
Polyhedron 68 (2014) 151–156

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Mn(II) complexes of three [2 + 2] macrocyclic Schiff base ligands. Synthesis and X-ray crystal structure of the first binuclear–di(binuclear) cocrystal

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ARTICLE INFO

Article history:
Received 6 August 2013
Accepted 23 September 2013
Available online 14 October 2013

Keywords:
Manganese(II)
Binuclear complexes
Di(binuclear)
Macrocylic Schiff base ligands
Cocrystal

ABSTRACT

The [2 + 2] cyclocondensation reactions of N-(2-pyridylmethyl)-N-(2-aminoethyl)-1,2-diaminoethane (L_{22py}), N-(2-pyridylmethyl)-N-(2-aminoethyl)-1,3-diaminopropane (L_{23py}) and N-(2-pyridylmethyl)-N-(3-aminopropyl)-1,3-diaminopropane (L_{33py}) with 2,6-diformyl-4-methylphenol (dfp) in the presence of $MnCl_2$ $4H_2O$ in equimolar ratios are reported. The resulting compounds, (**1**), (**2**) and (**3**), respectively, were characterized by IR spectroscopy, elemental analysis and mass spectrometry. The X-ray crystal structure analysis of (**3**) showed that it contains a novel cocrystal of a binuclear Mn(II) macrocyclic cation and a di(binuclear) one. The Mn(II) ions in the latter binuclear and di(binuclear) cations are five and six-coordinate respectively. The two binuclear parts in the di(binuclear) cation are bonded through two bridging chloride ions. The macrocyclic ligand in the above cations also has two different conformational structures, but in both cases it catches a proton. The analytical data show that compounds (**1**) and (**2**) probably have similar structures to (**3**).

1. Introduction

Dimerization of two binuclear metal complexes through suitable bridging groups leads to the formation of complexes of the type $[\{M_2(L)Y_n\}_2(\mu\text{-}X)_m]$, where M is a metal ion, L is a macrocyclic ligand capable of holding two metal ions, X is a bridging group and Y is the symbol for a coordinated solvent, anion, etc. There are a few examples of the dimerization of binuclear metal complexes in the literature [1–13] and we use here, for first time, the term "di(binuclear)" for such complexes. On the other hand, to the best of our knowledge, the cocrystallization of a di(binuclear) complex with a binuclear one has not been reported in the literature for any metal ion. Indeed, a literature review shows that there are only a limited number of reports for the characterization of cocrystals of metal complexes [14–21]. This paper deals with the synthesis and characterization of three Mn(II) macrocyclic Schiff base complexes that in one case, at least, show the cocrystallization of a di(binuclear) complex with a binuclear one. The latter complexes are products of the [2 + 2] cyclocondensation reaction of three tripodal tetraamines with 2,6-diformyl-4-methylphenol, dfp, in the presence of manganese chloride. Various amines have been involved in [1 + 1], [22–25] [2 + 2], [26–36] [2 + 3], [37–41] [3 + 3], [42] and [4 + 4], [43,44] Schiff base cyclocondensations with dfp. We were also interested in studying the cyclocondensation of symmetrical and asymmetrical tripodal tetramines bearing a pyridine group (see Fig. 1) with dfp in the presence of the Mn(II) metal ion. The [2 + 2] Schiff base cyclocondensation of one of these ligands, L_{33py}, in the presence of manganese(II) acetate has been already reported, [45] and we were interested to see whether our reactions could lead to the formation of different compounds. Although the results of our reactions are also a [2 + 2] Schiff base condensation (see Scheme 1 and Fig 2), we show that the structures of the resulting compounds are considerably different to the previously reported structure.

2. Experimental

2.1. General information

Hydrated manganese chloride was obtained from Aldrich and was used without further purification. The partially asymmetrical tripodal ligands L_{22py} and L_{33py} as well as the totally asymmetrical tripodal ligand L_{23py} were prepared as their hydrochloride salts *via* literature methods [46,47]. IR and UV spectra were measured on

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http://dx.doi.org/10.1016/j.poly.2013.09.036

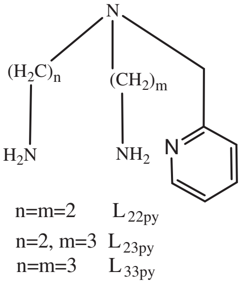
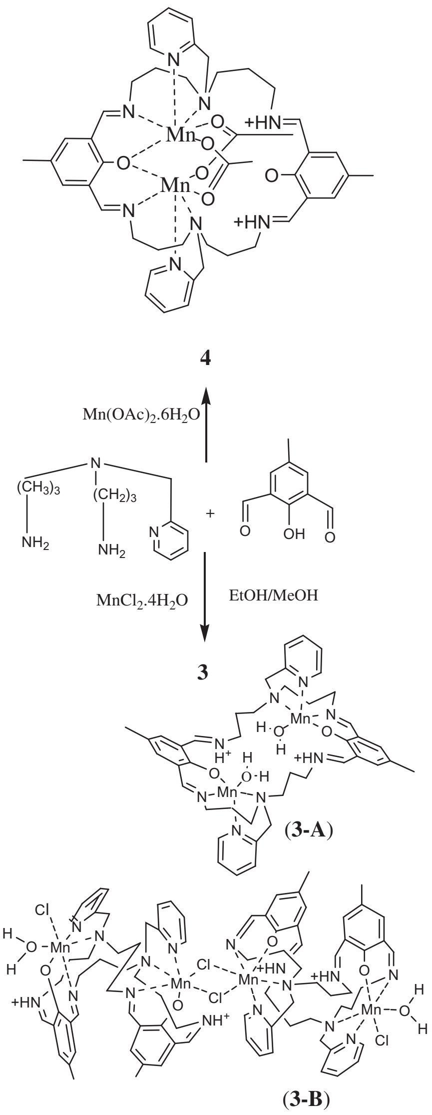


Fig. 1. Structure of the tripodal tetradentate ligands.

Perkin Elmer FT-IRGX and UV spectrophotometers. Mass spectra were measured on a Bruker micro TOFQ.

2.2. X-ray crystal structure determination

A summary of the details of the crystal data, data collection and refinement details are given in Table 1. The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation. For compound **3** a yellow prismatic crystal with dimensions of 0.27 × 0.09 × 0.04 mm was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 47917 unique reflections. Data were collected at a temperature of 293(2) K to a maximum 2θ value of 53.48°, in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [48] software package. The numerical absorption coefficient, μ, for Mo Kα radiation is 0.700 mm^{-1}. A numerical absorption correction was applied using X-RED [49] and X-SHAPE [50] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [51] and a subsequent difference Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [51]. All of the hydrogen atoms were located in ideal positions and then refined isotropically. Subsequent refinement then converged with R factors and parameter errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [52]. All refinements were performed using the X-STEP32 crystallographic software package [53].



Scheme 1. Synthetic routes to the cocrystal **3** and compound **4**, along with an illustration of the resulting macrocyclic Schiff base cations in their crystal structures.

2.3. Synthesis

2.3.1. Preparation of $[\{Mn_2(H_2L_1)Cl(H_2O)\}_2(\mu\text{-}Cl)_2][Mn_2(H_2L_1)(H_2O)_2](ClO_4)_6Cl_2$, **1**

$L_{22py}\cdot 3HCl$ (0.1 g, 0.33 mmol) and NaOH (0.04 g, 0.99 mmol) were mixed and heated under reflux for 30 min in EtOH (15 ml). The NaCl which formed upon cooling was filtered off. The filtrate was added to a mixed solution of 2,6-diformyl-4-methylphenol (0.05 g, 0.33 mmol) and $MnCl_2\cdot 4H_2O$ (0.06 g, 0.33 mmol) in dry MeOH (40 ml) with continuous stirring, and the solution colour gradually changed from brown to deep green. The mixture was stirred at room temperature for 72 h, then $NaClO_4$ (0.09 g, 0.66 mmol) was added. The solution was filtered and the filtrate was reduced to ca 10 cm^3. A yellow crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 40%. *Anal.* Calc. for $C_{114}H_{140}Cl_{12}Mn_6N_{24}O_{34}$: C, 43.82; H, 4.41; N, 10.77. Found: C, 43.18; H, 4.19; N, 10.56%. IR (KBr, cm^{-1}): 1623, ($\nu_{C=N}$ schiff base), 1558 ($\nu_{C=N}$ pyridine), 1568 ($\nu_{C=C}$), 1081. UV (acetonitrile, nm (ε, L mol^{-1} cm^{-1})): 228 (4690), 280 (3270). Accurate mass spectrometry (ESI-MS) *m*/*z*: 697.1471 [ML^+], $C_{38}H_{42}MnN_8O_2$ requires 697.2811; 787.1922 [M_2LCl^+], $C_{38}H_{42}ClMn_2N_8O_2$ requires 787.188; 822.0983 [$M_2LCl_2{}^+$], $C_{38}H_{42}Cl_2Mn_2N_8O_2$ requires 822.1568.

2.3.2. Preparation of $[\{Mn_2(H_2L_2)Cl(H_2O)\}_2(\mu\text{-}Cl)_2][Mn_2(H_2L_2)(H_2O)_2](ClO_4)_6Cl_2$, **2**

The yellow powder complex **2** was prepared in an analogous manner using $L_{23py}\cdot 3HCl$. Yield: (38%). *Anal.* Calc. For ($C_{120}H_{128}Cl_{12}Mn_6N_{24}O_{34}$): C, 47.11; H, 4.26; N, 10.92. Found: C, 46.69; H, 4.14; N, 10.76%. IR (KBr, cm^{-1}): 1628, ($\nu_{C=N}$ schiff base), 1552 ($\nu_{C=N}$ pyridine), 1566 ($\nu_{C=C}$), 1087. UV (acetonitrile, nm (ε, L mol^{-1} cm^{-1})): 232 (4686), 276 (3266). Accurate mass spectrometry (ESI-MS) *m*/*z*: 725.3119 [ML^+], $C_{40}H_{46}MnN_8O_2$ requires 725.3124; 815.2238 [M_2LCl^+], $C_{40}H_{46}ClMn_2N_8O_2$ requires 815.2193; 851.1991 [$M_2HLCl_2{}^+$], $C_{40}H_{47}Cl_2Mn_2N_8O_2$ requires 851.1960.

2.3.3. Preparation of $[\{Mn_2(H_2L_3)Cl(H_2O)\}_2(\mu\text{-}Cl)_2][Mn_2(H_2L_3)(H_2O)_2](ClO_4)_6Cl_2$, **3**

The yellow powder complex **3** was prepared in an analogous manner using $L_{33py}\cdot 3HCl$. Yield: (50%). *Anal.* Calc. For ($C_{126}H_{164}Cl_{12}Mn_6N_{24}O_{34}$): C, 45.74; H, 4.78; N, 10.19. Found: C, 45.48; H, 4.57; N, 9.89%. IR (KBr, cm^{-1}): 1627, ($\nu_{C=N}$ schiff base), 1560 ($\nu_{C=N}$ pyridine), 1565 ($\nu_{C=C}$), 1089. UV (acetonitrile, nm (ε, L mol^{-1} cm^{-1})):