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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
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To cite this Article De Sànchez, Amanda Reyes , Anacona, Juan Roberto and Màrquez, Victoria Elena(1994) 'Synthesis and properties of transition metal complexes with a novel tetradentate macrocyclic ligand containing 1,10-phenanthroline derivatives', Supramolecular Chemistry, 4: 1, 9 — 12

To link to this Article: DOI: 10.1080/10610279408029856

URL: http://dx.doi.org/10.1080/10610279408029856

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SUPRAMOLECULAR CHEMISTRY, Vol. 4, pp. 9–12
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Synthesis and properties of transition metal complexes with a novel tetradentate macrocyclic ligand containing 1,10-phenanthroline derivatives

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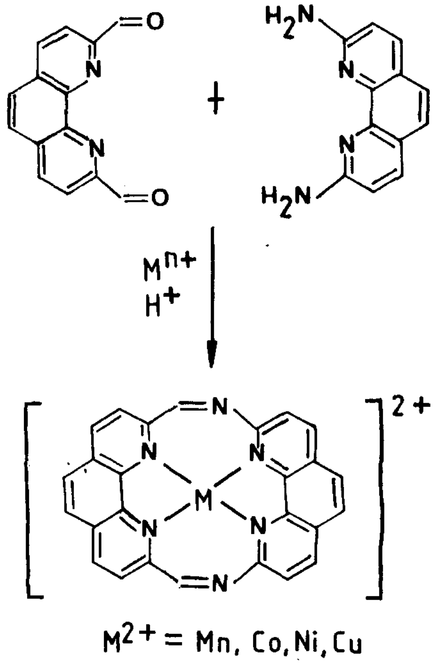
(Received February 9, 1993)

Complexes of a tetradentate macrocyclic ligand L with manganese(II), cobalt(II), nickel(II) and copper(II) ions have been prepared by condensation of 2,9-diamino-1,10-phenanthroline and 1,10-phenanthroline-2,9-dicarboxaldehyde in the presence of metal ion templates. Electrical conductivity measurements, ir and ^{1}H NMR spectral data are reported and evaluated to show that ring closure rather than polymer formation has occurred. The template condensation in the presence of chromium(III) chloride and hydrochloric acid (pH = 1) leads to the formation of the free macrocycle rather than the expected metal complex.

INTRODUCTION

It has been demonstrated by the Lewis group[1–21] that complexes of planar tetradentate or pentadentate macrocyclic ligands incorporating 1,10-phenanthroline may be prepared by the template condensation of suitable dicarbonyl compounds with bis(hydrazine)-substituted heterocyclic compounds. Template condensations are very satisfactory methods for the preparation of macrocyclic complexes, but they are sensitive to the metal ion which is used to direct the reaction.

Recently, azamacrocyclic systems have been intensively investigated in attempts to correlate their electronic properties and reactivities with those of polypyrrolic macrocycles. Ogawa *et al.*[22–24] have reported the non-template preparations of free macrocycles of diethenotetrapyridohexa-azacyclotetradecines with high yield by condensing 2,9-dimethyl-1,10-phenanthroline with 2,9-dichloro-1,10-phenanthroline or 2,9-diamino-1,10-phenanthroline with 2,9-dichloro-1,10-phenanthroline or 2,9-diamino-1,10-phenanthroline alone under heating. As we are undertaking a systematic study of the synthesis and electrochemistry of the complexes of macrocyclic ligands containing heterocycles with nitrogen, due to the possibility that the complexes may reflect some of the electrochemical features associated with the simpler complexes of phenanthroline, we propose to study the template synthesis and characterization of manganese(II), cobalt(II), nickel(II) and copper(II) complexes of a new hexa-azamacrocyclic ligand L obtained by condensation of 2,9-diamino-1,10-phenanthroline and 1,10-phenanthroline-2,9-dicarboxaldehyde by the reaction scheme below.



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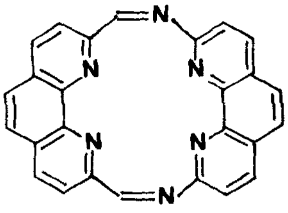
OR

(L)



IF M = Cr(III)

RESULTS AND DISCUSSION

When 2,9-diamino-1,10-phenanthroline and 1,10-phenanthroline-2,9-dicarboxaldehyde are refluxed in hot aqueous methanolic solution, in the presence of several drops of dilute hydrochloric acid (pH = 1) and under nitrogen atmosphere during 12 h, a yellow precipitate of L is obtained in 60% yield. A slightly better yield of L is obtained when chromium(III) is used as template[1] along with hydrochloric acid. Metal complexes are obtained when manganese(II), cobalt(II), nickel(II) or copper(II) react with the free macrocycle or by *in situ* preparation with the phenanthroline derivatives. The complexes appear to be stable. Attempts to prepare metal complexes by reacting free macrocycle with zinc(II), palladium(II) or platinum(II) ions were unsuccessful probably due to kinetic effects and/or problems forming a transition state with the less accommodating heavy metal ions. In the absence of a template ion, predominantly polymeric products are obtained.

Infrared spectroscopy provides valuable information as to whether or not condensation to form hydrazone bonds has occurred. The diketones produce bands close to 1700 cm^{-1} while the terminal NH_2 groups of the hydrazines give N—H stretching vibrations[25] at 3300 and 3200 cm^{-1}, and the N—H bending mode is at 1630 cm^{-1}. The hydrazone band, at 1650 cm^{-1}, does not overlap with the above bands and simple observation of the 1600–1750 cm^{-1} region indicates the success or failure of a reaction. The spectra of the studied metal(II) complexes show significant bands from 1600 to 1640 cm^{-1} which may be assigned to ν(C=N) stretching modes. A broad, diffuse band of medium intensity in the 3500–3300 cm^{-1} region may be assigned to the O—H stretching vibration for lattice water.[26] A weak absorption found at 530 cm^{-1} may suggest the presence of coordinated water.[27] A strong band, the C—H deformation, is always seen from 820 to 850 cm^{-1}.[28] The absence of bands characteristic of carbonyl and amine groups strongly suggests that ring closure rather than polymeric compounds have been formed. Infrared data, elemental analysis and molar conductivities for the complexes prepared can be appreciated in Table 1.

As it has been noted before[19] a polymer consisting of n units will have 2n + 1 ions present (2n anions and one large cation) and a molar conductivity corresponding to a 2:1/n electrolyte. As n has to be large, the conductivity of a polymer species should be lower than that predicted for the macrocyclic species. The experimental values in Table 1, measured on 10^{-3} mol dm^{-3} solutions in DMSO at room temperature, fall in the range 2:1 electrolytes for the manganese, cobalt and nickel complexes and in the range of a 1:1 electrolyte for the copper complex attending the criteria of Geary,[29] thereby demonstrating the presence of a cyclic ligand.

The mass spectrum of the free macrocycle does contain a peak corresponding to the parent ion (m/e 410). Mass spectra of metal complexes using the direct probe electron impact technique did not provide direct confirmation of the presence of the macrocycles since no parent ions peak were observed, only those due to macrocycle fragments.

The ^1H NMR spectra of the free macrocycle was

Table 1 Infrared data, elemental analysis and molar conductivities

			Infrared data[a]			*Analysis*[b]			Λ[c]
Complex	*Color*	*νC=N*	*νC=C*	*δC—H*	*δC—H*	*%C*	*%H*	*%N*	(S cm^{-1} mol^{-1})
(L).2HCl	light yellow	1650	1580	1250	850	64.24 (64.60)	3.35 (3.31)	17.19 (17.39)	
|Mn(L)|.2Cl.3H$_2$O	brown	1600	1560	1230	825	52.52 (52.88)	3.52 (3.39)	14.43 (14.24)	77.4
|Co(L)|.2Cl.5H$_2$O	green	1635	1530	1208	820	49.85 (49.53)	3.65 (3.81)	13.01 (13.33)	65.0
|Ni(L)|.2Cl.4H$_2$O	yellow	1620	1550	1210	840	50.78 (51.00)	3.83 (3.60)	14.05 (13.73)	67.0
|Cu(L)|.2Cl.4H$_2$O	green	1640	1550	1205	820	50.35 (50.60)	3.49 (3.57)	13.47 (13.62)	31.8

[a] Nujol mulls on a Perkin-Elmer 567. Frequencies are in cm^{-1} and calibrated against polystyrene.
[b] Calculated values are given in parentheses.
[c] Measured at room temperature on solutions 10^{-3} mol dm^{-3} in DMSO.

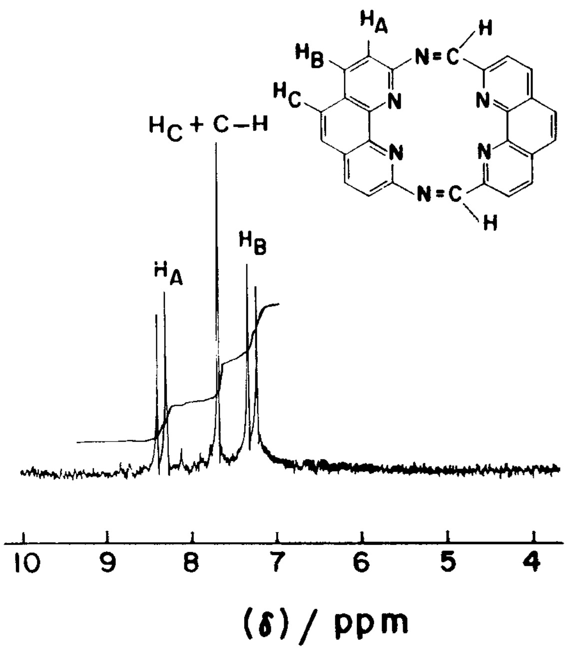


Figure 1 ¹H NMR spectrum of free macrocycle L.

run at 80 MHz with TMS as internal standard in DMSO solution. The aromatic region of phenanthroline has been thoroughly investigated in a variety of solvents[30–32] and Carman and Hall[30] have been able to assign the various signals unambiguously to individual hydrogen atoms on the rings. Thus, three absorptions were observed in the 7.0–8.5 ppm range. H_A and H_B form an AB spin system and the hydrogen atom pattern is a doublet of doublets, as is evident in Fig 1. H_C atoms are equivalent nuclei and they are superimposed with the C—H signal. The integrated relative intensities of the above signals: H_A, H_C, H_B, were in good agreement with the required ratio of 2:3:2, respectively.

The ultraviolet spectrum (200–900 nm region) of the free base which gives a yellow solution in methanol, presents two bands at 316 and 380 nm which can also be appreciated in all metal complexes. If these macrocycles are compared with the spectrum of phenanthroline itself it is clear that the macrocycles cannot be treated as two phens isolated from each other and for the purposes of comparison it should be remembered that there will be a bathochromic shift due to ring substitution in addition to a hypsochromic shift upon coordination. The slightly bathochromic shift (~20 nm) of free base with respect to the phenanthroline-containing hexa-azamacrocycles of Ogawa can be attributed to more effective electron delocalisation in the former. Because of the high degree of unsaturation of the macrocyclic ligand, the intense ultraviolet absorptions have tails in the visible region of the spectrum and this makes it difficult to identify accurately the positions of the weak d-d transitions when they can be observed. The only d-d transitions observed were for the Cu(II) complex at 450 nm in methanol and at 395 nm in DMSO for the Ni(II) complex suggesting in the latter case a low spin state, but such information was not revealed by NMR data. The cobalt(II) complex show two absorptions at 667 and 600 nm in DMSO, suggesting octahedral or pseudooctahedral geometry in this solvent.

Since none of these complexes have been prepared prior to this work there is no structural information concerning them. On the assumption that four nitrogen atoms of the macrocycles are coordinated to the metal, as seems likely from an inspection of molecular models and as found previously for 2,2′-bipyridine complexes of the N_4 rings so far analysed by X-ray diffraction methods,[2–6] it follows that the present complexes contain four-coordinate Mn(II), Co(II), Ni(II) or Cu(II). From models it appears that both a planar or approximately planar configuration of the macrocycle are possible but without a full structural analysis one cannot make a distinction between these possibilities. Despite the crystalline nature of the products, none proved suitable for X-ray structure determination. In the absence of X-ray structural data for these complexes it is difficult to assign their solid state structure, but it may well involve coordination of both chloride ions to the metal.

EXPERIMENTAL

Infrared spectra of Nujol mulls supported between sodium chloride discs were recorded using a Perkin-Elmer 567 spectrometer, over the range 600–4000 cm^{-1}. Conductance measurements were made with a Wayne-Kerr Universal bridge. The ¹H NMR spectrum was run at 80 MHz on a Varian spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc. Mass spectra were run using a Hewlett-Packard spectrometer between 100–220 °C over the range 32–800 uma. Ultraviolet spectra were recorded using a Varian DMS 80 spectrometer over the range 200–900 nm.

Reagents of analytical grade where possible were used without further purification. All solvents used were distilled, dried, and degassed before use and all preparations were carried out under a nitrogen atmosphere.

2,9-diamino-1,10-phenanthroline and 1,10-phenanthroline-2,9-dicarboxaldehyde were synthesized from 2,9-dichloro-1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline, respectively, from published methods.[23,33] 2,9-dichloro-1,10-phenanthroline was prepared by the procedure described previously[20] and

2,9-dimethyl-1,10-phenanthroline was obtained from Aldrich.

[Mn(L)].2Cl.3H_2O

An example of the general preparative method for these complexes is the synthesis of the manganese(II) complex of L. To a refluxing solution of 2,9-diamino-1,10-phenanthroline (0.08 g, 0.38 mmol) in methanol (10 cm^3) a solution of $MnCl_2.4H_2O$ (0.075 g, 0.38 mmol) in methanol (5 cm^3) was added slowly, followed by 1,10-phenanthroline-2,9-dicarboxaldehyde (0.09 g, 0.38 mmol) in methanol (10 cm^3). The refluxing continued for 12 h, and then the solution was evaporated on a rotary evaporator. After cooling, the solid present was filtered off and washed with water and methanol and dried *in vacuo*. Yield: 65%.

(L).2HCl

To a refluxing solution of 2,9-diamino-1,10-phenanthroline (0.035 g, 0.16 mmol) in methanol (10 cm^3) made acidic (pH = 1) by adding drops of hydrochloric acid, was added dropwise 1,10-phenanthroline-2,9-dicarboxaldehyde (0.04 g, 0.16 mmol) in methanol (20 cm^3). The solution was refluxed and stirred 12 h, during which the yellow product precipitated. The product was isolated, washed with hot methanol and dried *in vacuo* at room temperature over P_2O_5. Yield: 60%. Alternatively this compound could be obtained in 70% yield from the diamine, dicarbonyl, and $CrCl_3.6H_2O$ (1:1:1 molar ratio). The purity of the product was controlled by thin layer chromatography and where appropriate it was filtered through a column of silica gel (25 g) with ethanol-25% NH_4OH (1:1 v/v) as eluent to give a yellow solid.

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