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Precursors of aza-macrocycles: Characterization of substituted phenanthrolines and related bases. Crystal and molecular structure of dichloro-di-*n*-butyl(2,2′,6,6′-bipyrimidine)-tin(IV)

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Abstract

The synthesis, characterization and ^{1}H NMR spectra of some substituted 1,10-phenantrolines are described. These are precursors of azacyclophanes which are, along with their metal complexes, insoluble in polar solvents. It is suggested that the use of substituted 2,2′,6,6′-bipyrimidines as precursors would lead to soluble macrocycles.
The crystal and molecular structure of dichloro-di-n-butyl-(2,2′,6,6′-bipyrimidine) tin(IV) shows this ligand to be planar and bidentate.

INTRODUCTION

Several literature reports have proposed that the transformation of carbon dioxide into organic substrates can be used as a cheap source of fuels and chemicals (refs. 1-4).

The reduction of carbon dioxide can be driven electrochemically (refs. 5-9) or photochemically (refs. 10-14). In the electrochemical reduction over metallic cathodes, the large overpotential required for driving the electrode reaction at an appropriate rate is an unquestionable technical problem which has been addressed by adding catalysts to the reaction (refs. 10, 15-18). A similar strategy can be applied to the photoreduction of carbon dioxide in homogeneous solutions.

Tetra-aza-macrocyclic and related complexes of cobalt and nickel have been successfully used as catalysts in electrochemical and photochemical procedures (refs. 19-22). However, little is known about the properties of macrocyclic compounds derived from 1,10-phenanthroline and related bases(refs. 23-29). Since these compounds can be considered relatives of the phthalocyanines and porphyrins, they have potentially interesting chemical properties as catalysts in processes useful for the preparation of fuels and/or the storage of solar energy.

The present work shows the synthesis, characterization and structural properties of precursors of azacyclophanes and related macrocycles. One additional goal of these preparations is the obtention of presently non-commercial compounds in good yields.

EXPERIMENTAL

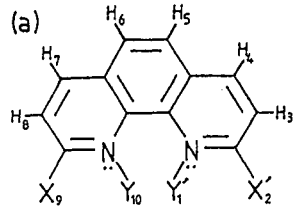
Phenanthroline and bipyrimidine were commercially available. Precursors I to V, Fig. 1 were synthesized according to techniques reported in the literature (refs. 26, 29) with some modifications to rigorously exclude moisture from the reactions; infrared spectra were recorded on a Bruker, model IFS-66V spectrometer in KBr pellets; nucler magnetic resonance spectra of protons were taken on a Bruker model AC-200P spectrometer in $CDCl_3$ at room temperature. TMS was used as an internal standard. Melting points were not corrected.

Dichloro-di-n-butyl(2,2',6,6'-bipyrimidine) tin(IV) was obtained as a colorless crystalline solid by refluxing stoichiometric amounts of dichlorodi-n-butyltin(IV) and 2,2',6,6'-bipyrimidine in cyclohexane. The solid was recrystallized from dichloromethane:cyclohexane 1:1 (v/v), giving monoclinic crystals, mp. 104-107°C. Analytical, thermogravimetric and spectroscopic data confirm the proposed composition (ref. 30). X-ray intensities were collected with a R3 Nicolet diffractometer.

RESULTS AND DISCUSSION

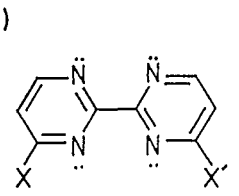
Synthesis and characterization of some precursors. The structures of the macrocyclic ligands, X, XI and XII derived from (substituted) phenanthrolines (I to VI) and bipyrimidines (VII to IX) are shown in Fig. 1. Little is known about the properties of these macrocycles and their complexes. Synthetic methods were earlier reported by Ogawa and Lewis (refs. 24-26, 29); the cumbersome multistep syntheses produce the ligands with extremely low yield, i.e. <1%. This synthetic problem has limited work with these compounds to the determination of a few spectra (refs. 27, 28).

(a)



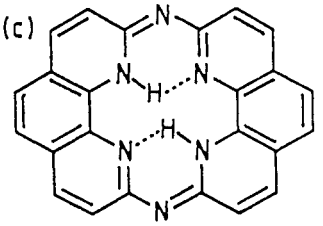
I - VI

(b)



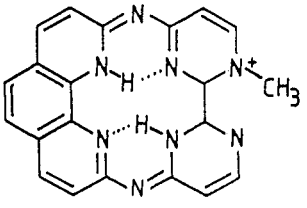
VII - IX

(c)

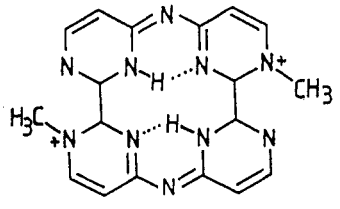


X

(d)



XI



XII

	X	Y	Y'	X'
I(e)	H	-	CH_3	Ar=O
II	H	-	-	Cl
III	H	N^+-CH_3	-	Cl
IV (f)	Ar=O	CH_3	-	Cl
V	Cl	-	-	Cl
VI	NH_2	-	-	NH_2
VII	H	-	-	H
VIII	Cl	-	-	Cl
IX	NH_2	-	-	NH_2

Figure 1. (a) derivatives of phenanthroline (I-VI); (b) derivatives of bipyrimidine (VII-IX); (c) water insoluble macrocycle (X); (d) water soluble macrocycles(XI, XII); (e) 1-methyl-1,10-phenantrolin-2-one; (f) 2-chloro-10-methyl-1,10-phenantrolin-9-one.

TABLE 1. ^{1}H-NMR Data[a] of some of the precursors shown in Fig. 1.

COMP.	H_9	H_8	H_7	H_6	H_5	H_4	H_3	CH_3
I	8.94(dd)	7.49(q)	8.17(dd)	7.56(s)	7.56(s)	7.78(d)	6.90(d)	4.48(s)
		(8.2)	(8.2)			(10.0)	(10.0)	
	(4.0)	(4.0)						
	(2.0)		(2.0)					
II	9.21(dd)	7.64(q)	8.25(dd)	7.76(d)	7.81(d)	8.18(d)	7.62(d)	--
		(8.1)	(8.1)	(8.8)	(8.8)	(8.4)	(8.4)	
	(4.3)	(4.3)						
	(1.7)		(1.7)					
III	9.29(d)	8.29(q)	9.16(d)	8.09(s)	8.09(s)	8.38(d)	7.78(d)	5.12(s)
		(8.3)	(8.3)					
	(6.0)	(6.0)						
IV	--	7.50(d)	8.15(d)	7.56(d)	7.63(d)	7.79(d)	6.94(d)	4.44(s)
		(8.5)	(8.5)	(8.4)	(8.4)	(9.3)	(9.3)	
V	--	7.66(d)	8.22(d)	7.84(s)	7.84(s)	8.22(d)	7.67(d)	--
		(8.3)	(8.3)			(8.3)	(8.3)	

[a]: values, in ppm; ( ): coupling constants, in Hz; (d): doublet; (dd): doublet of doublet; (q): quadruplet; (s): singlet.

Table 1 shows the ^{1}H-NMR data of precursors **I** to **V**, Fig. 1, which have been obtained in high yields in extremely dry conditions. These spectra, and infrared and analytical results, confirm their formulae. Precursors **II** and **V** are not commercially available; their importance is associated with diverse possibilities of synthesing other derivatives.

A future goal of these preparations is to obtain complexes of appropriate metals with macrocycles such as those shown in Fig. 1(c) in high yields. Also, it is of particular interest to establish the nature of the redox processes to characterize the multiple electron transfers involving either or both the metal center and the ligand as in the case of the phthalocyanines. It must be noticed that the macrocyclic products of the multiple reductions may have also important properties compared to the starting materials (refs. 31, 32).

However, one significant difficulty is related to the insolubility of these kind of ligands and their complexes in polar solvents. Small variations in the synthesis of the macrocyclic **X** could lead to the macrocycles **XI** and **XII** which are indeed soluble (ref. 33). This modification consists of the use of the precursors **VIII** (dichloro-bipyrimidine) and **IX** (diammine-bipyrimidine), both obtainable from **VII** (bipyrimidine). This is an open area of synthesis.

The crystal and molecular structure of dichlorodi-n-butyl(2,2',6,6'-bipyrimidine)tin(IV). Complexes of general formula $R_2SnX_2L_n$, where L is a N-donor aromatic base and X is Cl or Br, have been synthesized recently. The molecular structures are strongly influenced by the anion (ref. 34). The crystal and molecular structure of dichlorodi-n-butyl (2,2',6,6'-bipyrimidine) tin(IV) is shown in this work.

Table 2 contains general crystallographic data obtained for the compound. During the refinement stage some disorder appeared in the terminal carbon atoms of the butyl groups. This kind of phenomenon has been previously observed for analogous structures(ref. 35). Fixed models and a lowering of the occupancy of these atoms have been employed in order to overcome this problem.

TABLE 2. General Crystallographic Data for Dichlorodi-n-butyl(2,2',6,6'-bipyrimidine) tin(IV).

Formula	$SnCl_2C_{16}N_4H_{24}$
F_w	928
a(Å)	10.885
b(Å)	10.839
c(Å)	17.800
β(°)	106.3
V(Å^3)	2015.677
Z	4
D_c(g/cm^3)	1.523
Space Group	$P2_1/c$
Radiation	Mo Kα
Crystal Dimensions(mm)	0.40x0.30x0.20
Scan Mode	θ-2θ
2-θ Limits(°)	3-60
Number of Reflections	3757
Observed Reflections	2411
Number of Variables	230
Final R(R_w)	0.065 (0.093)

The molecular structure of the title compound, which includes the thermal ellipsoids, is shown in Fig. 2. The following was observed: the geometry around tin is pseudo-octahedral; chlorine atoms are in cis positions with butyl groups trans; 2,2',6,6'-bipyrimidine is essentially planar and is acting as a bidentate ligand in this case. It has been

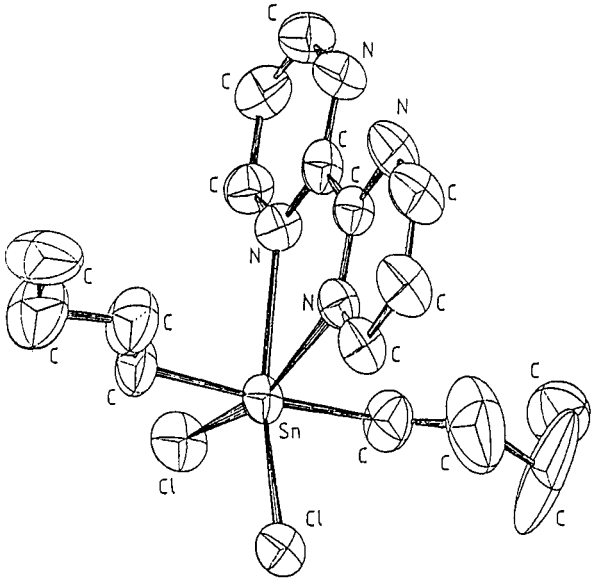


Figure 2. Molecular structure for dichlorodi-n-butyl(2,2',6,6' bipyrimidine) tin(IV), $Sn(IV)Cl_2(C_4H_9)_2(C_8H_6N_4)$

recently found a dimer of tin(IV), namely dichlorodiethyltin(IV)-μ-(2,2',6,6'-bipyrimidine) dichlorodiethyltin(IV), in which bipyrimidine tetradentate (ref. 36).

Figure 3 shows the packing structure for several neighboring cells. It is possible to observe the closeness between butyl groups of adjacent molecules and the planarity of the bipyrimidine ligands.

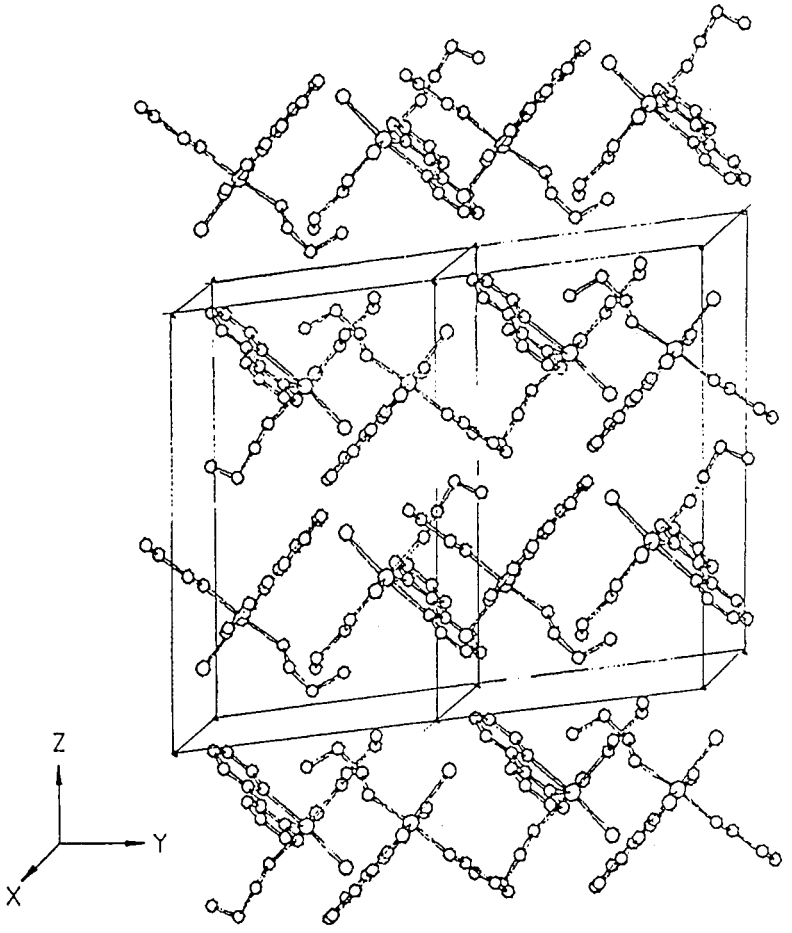


Figure 3. Crystal packing for dichlorodi-n-butyl(2,2',6,6'-bipyrimidine) tin(IV), $Sn(IV)Cl_2(C_4H_9)_2(C_8H_6N_4)$.

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