

## Silver(I) and Cadmium(II) Complexes of Pentadentate Macrocyclic Ligands Containing Phosphorus Donor Atoms\*

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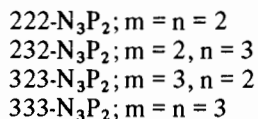
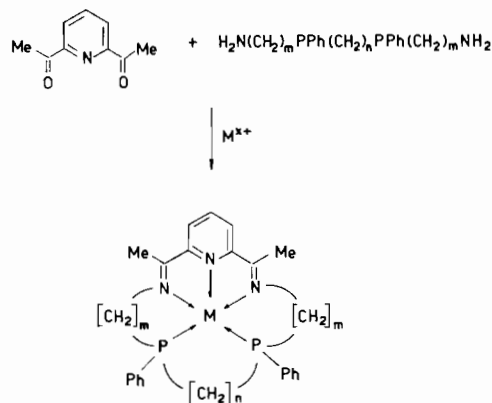
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The condensation of primary amines with aldehydes or ketones in the presence of metal ions has been extensively investigated in recent years. Such reactions, under the influence of the template effect, have produced many synthetic macrocycles containing nitrogen donor atoms [1]. Many mixed donor nitrogen–oxygen and nitrogen–sulphur macrocycles have also been prepared but there appear to be only two reports [2] of the incorporation of a (single) phosphorus atom into a macrocyclic ligand. The introduction of more than one phosphorus atom into macrocyclic ligands is of potential interest in view of the known ability of phosphorus to stabilize low oxidation states. This property, in combination with the special properties [3] of macrocyclic ligands, makes the attempt to synthesize ‘phosphorus macrocycles’ an attractive one. As a first step in this endeavour we have investigated the effectiveness of a range of metal ions in promoting the synthesis of pentadentate ‘N<sub>3</sub>P<sub>2</sub>’ macrocycles. This class of macrocycle was chosen for initial study because of the successful synthesis of a variety of ‘N<sub>5</sub>’, ‘N<sub>3</sub>O<sub>2</sub>’ and ‘N<sub>3</sub>S<sub>2</sub>’ rings via the Schiff base condensation of 2,6-diacetylpyridine with the appropriate tetrafunctional di-primary amine [4]. Thus, the incorporation of two phosphorus atoms into rings of this class appeared possible using well established synthetic routes.

### Experimental

The template synthesis of the four mixed nitrogen–phosphorus macrocycles 222-N<sub>3</sub>P<sub>2</sub>, 232-N<sub>3</sub>P<sub>2</sub>, 323-N<sub>3</sub>P<sub>2</sub> and 333-N<sub>3</sub>P<sub>2</sub> by the reaction scheme shown was attempted.

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The ditertiaryphosphinodiamines were prepared in two-step syntheses from phenylphosphine, and the appropriate chloroamines and dichlorides by methods described by Isslieb [5] and characterized by elemental analysis and mass spectra. Reactions of the diphosphinodiamines with 2,6-diacetylpyridine and the perchlorates of Mn(II), Fe(II), Zn(II), Cd(II), Hg(II) and Ag(I) were carried out in refluxing methanol (1:1:1 molar proportions) for periods varying from 4–16 h. At the end of the reaction period the hot solution was filtered free from any solid material present and allowed to concentrate to yield product. This was separated and examined by i.r. spectroscopy and chemical analysis. If these preliminary results indicated that a metal macrocycle complex might have been formed the crude product was recrystallized from methanol, ethanol or acetonitrile and subjected to further physico-chemical tests (see below). The original filtrate was further concentrated and solid fractions recovered from this were examined in similar fashion.

### Results and Discussion

In every case i.r. spectra indicated Schiff base formation on reaction, as judged by the occurrence of a  $\nu(\text{C}=\text{N})$  absorption at  $\sim 1650 \text{ cm}^{-1}$ . However, most of the materials isolated also exhibited a band at  $\sim 1700 \text{ cm}^{-1}$  attributable to  $\nu(\text{C}=\text{O})$  of unreacted keto groups. With the exceptions to be discussed below the products were amorphous solids which gave rather broad i.r. spectra and variable chemical analyses. Although poorly soluble in water, ethanol and in most other organic solvents they could usually be ‘recrystallized’ from methanol or acetonitrile.

TABLE. Yields, Analytical and Electrical Conductance Data for the Complexes.

Complex	Yield (%)	Analysis (%)						$\Lambda^a$ (S cm <sup>-1</sup> mol <sup>-1</sup> )
		Found			Calc.			
		C	H	N	C	H	N	
[Ag(323-N <sub>3</sub> P <sub>2</sub> )] ClO <sub>4</sub>	10–15 <sup>b</sup>	50.1	5.1	6.0	49.8	5.1	5.7	136
[Ag(323-N <sub>3</sub> P <sub>2</sub> )] BPh <sub>4</sub>	<sup>c</sup>	69.6	6.1	4.6	69.5	6.1	4.3	75
[Ag(333-N <sub>3</sub> P <sub>2</sub> )] ClO <sub>4</sub>	50–70 <sup>b</sup>	50.8	5.3	5.9	50.6	5.2	6.2	130
[Ag(333-N <sub>3</sub> P <sub>2</sub> )] BPh <sub>4</sub>	<sup>c</sup>	69.8	6.2	4.5	69.4	6.3	4.1	80
[Cd(323-N <sub>3</sub> P <sub>2</sub> )] (ClO <sub>4</sub> ) <sub>2</sub>	15–25 <sup>b</sup>	43.6	4.4	5.2	43.2	4.5	5.1	270
[Cd(323-N <sub>3</sub> P <sub>2</sub> )] (BPh <sub>4</sub> ) <sub>2</sub>	<sup>c</sup>	74.6	6.1	3.4	73.8	6.1	3.3	250
[Cd(333-N <sub>3</sub> P <sub>2</sub> )] (ClO <sub>4</sub> ) <sub>2</sub>	20–30 <sup>b</sup>	44.3	4.6	5.2	44.7	4.8	5.8	266
[Cd(333-N <sub>3</sub> P <sub>2</sub> )] (BPh <sub>4</sub> ) <sub>2</sub>	<sup>c</sup>	74.8	6.2	3.3	72.4	6.5	2.9	243

<sup>a</sup>10<sup>-3</sup> M in acetonitrile.  
methanol solution.

<sup>b</sup>Range observed in several preparations.

<sup>c</sup>Virtually quantitative from perchlorate complex in

However, little alteration in the relative intensities of the  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{O})$  bands was observed, nor any appreciable improvement in physical appearance. From these observations and in the light of experience gained earlier in the synthesis of the 'N<sub>5</sub>' macrocycles [4] it was concluded that these materials were metal complexes, of variable composition, of oligomers or mixtures of oligomers containing residual unreacted carbonyl groups.

Exceptions to these observations were obtained for the products of reactions of 2,6-diacetylpyridine with the two longest chain diphosphinodiamines in the presence of Ag(I) or Cd(II) and in these cases we believe that complexes of the macrocyclic ligands 323-N<sub>3</sub>P<sub>2</sub> and 333-N<sub>3</sub>P<sub>2</sub> have been formed (see Table). This conclusion is based on (i) the crystalline nature of the products,\* (ii) the absence of  $\nu(\text{C}=\text{O})$  and  $\nu(\text{N}-\text{H})$  absorption at  $\sim 1700$  and  $3100\text{--}3400$  cm<sup>-1</sup>, respectively, in i.r. spectra, (iii) the occurrence of  $\nu(\text{C}=\text{N})$  at  $\sim 1650$  cm<sup>-1</sup> along with the expected pyridine ring deformation bands at  $1400\text{--}1600$  cm<sup>-1</sup>, (iv) satisfactory chemical analysis, (v) the successful formation by metathesis of tetraphenylborate derivatives also meeting the above criteria, and (vi) reproducibility of the above.

Mass spectra provided no direct confirmation of the presence of the macrocycles since no parent ions peaks were observed, only those due to macrocycle fragments. Low solubility in suitable solvents precluded the determination of <sup>1</sup>H n.m.r. spectra except for Ag(333-N<sub>3</sub>P<sub>2</sub>)(ClO<sub>4</sub>), Cd(323-N<sub>3</sub>P<sub>2</sub>)(ClO<sub>4</sub>)<sub>2</sub> and Cd(333-N<sub>3</sub>P<sub>2</sub>)(ClO<sub>4</sub>)<sub>2</sub> in DMSO-d<sub>6</sub>. The spectra obtained, while not proving macrocycle formation, were at least consistent with it. In each case five distinct regions of absorption were observed — at 8.1–8.7(m), 7.3–7.4(m), 3.6–3.7(m), 2.0–2.3(m)

and 2.1–2.7(s) ppm. The integrated relative intensities were in good agreement with the required ratios of 3:10:8:8:6 and 3:10:8:10:6 for 323-N<sub>3</sub>P<sub>2</sub> and 333-N<sub>3</sub>P<sub>2</sub>, respectively, consistent with assignment of the signals to protons of the pyridine ring, phenyl rings, methylene groups adjacent to phosphorus, the remaining methylene groups, and the methyl groups.

In the mull i.r. spectra of the perchlorate complexes no splitting of the degenerate asymmetric stretching ( $\nu_3$ ) and bending ( $\nu_4$ ) modes of the ClO<sub>4</sub><sup>-</sup> ion was observed [6]. These occur as single bands at 1190 and 620 cm<sup>-1</sup>, respectively, with band widths no greater than those observed in reference complexes known to contain ionic ClO<sub>4</sub><sup>-</sup>. We infer, therefore, that all the compounds listed in the Table are salts of the complex cations [Ag(macrocycle)]<sup>+</sup> or [Cd(macrocycle)]<sup>2+</sup>. Electrical conductances for both the ClO<sub>4</sub><sup>-</sup> and BPh<sub>4</sub><sup>-</sup> derivatives in acetonitrile fall in the expected ranges [7] for 1:1 and 2:1 electrolytes, respectively (see Table).

On the assumption that all five donor atoms of the macrocycles are coordinated to the metal, as seems likely from an inspection of molecular models and as found previously for all complexes of the 'N<sub>5</sub>', 'N<sub>3</sub>O<sub>2</sub>' and 'N<sub>3</sub>S<sub>2</sub>' rings so far analysed by X-ray methods [4, 8], it follows that the present complexes contain five-coordinate Ag(I) or Cd(II). From models it appears that both an approximately planar and a folded conformation of the macrocycle are possible but without a full structural analysis a distinction between these possibilities cannot be made. We have previously described [8] the complex [Ag(323-N<sub>5</sub>)] ClO<sub>4</sub> in which the five nitrogens of the 17-membered ring lie in an approximate pentagonal plane and a similar structure has more recently been found [9] also for [Ag(323-N<sub>3</sub>S<sub>2</sub>)] BPh<sub>4</sub>. The present complexes extend the number of examples of this novel structural class.

\*None proved suitable for X-ray structure determination.

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