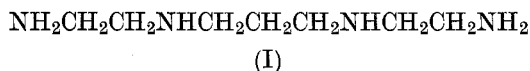


# AN OCTAMINE WHICH FUNCTIONS AS A BIS-QUADRIDENTATE LIGAND\*

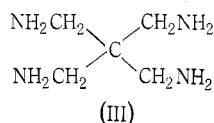
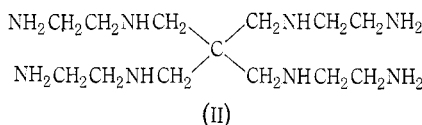
By A. T. PHILLIP†

In recent publications,<sup>1-3</sup> studies have been reported on the ligand 1,9-diamino-3,7-diazanonane (ETE; I)



which is a higher homologue of the well-known ligand triethylene tetramine.<sup>4-6</sup> In the transition metal complexes of (I), it was found that the four donor nitrogen atoms were either coplanar or arranged in a *cis* configuration around octahedral complex ions. This behaviour has been ascribed<sup>1,2</sup> to the increased flexibility of the organic molecule containing the central trimethylene chain.

A compound which has this molecular feature and has, in addition, the ability to form disymmetric, polynuclear coordination compounds is the octamine 6,6-bis(2',5'-diazapentyl)-1,4,8,11-tetraazaundecane (II).



This molecule may be regarded as two molecules of ETE which have been fused so that they have one common central carbon atom. A structurally related ligand, 2,2-bis(aminomethyl)-1,3-diaminopropane (III) has been studied by Bailar and Oehmke,<sup>7</sup> who obtained solid polymeric complexes of indeterminate structure, having the composition  $(\text{MLCl}_2)_n$ ,  $(\text{ML}_{1.5}\text{Cl}_2)_n$ , or  $(\text{M}_2\text{LCl}_4)_n$ .

We find that the octamine (II) forms a violet crystalline copper(II) complex of composition  $(\text{Cu}_2\text{LI}_4)$ , whose visible absorption maximum occurs at 523 nm

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<sup>1</sup> Phillip, A. T., Ph.D. Thesis, University of Sydney, 1964.

<sup>2</sup> Bosnich, B., Gillard, R. D., and McKenzie, E. D., *J. chem. Soc. (A)*, 1966, 1331.

<sup>3</sup> Hamilton, H. G., and Alexander, M. D., *J. Am. chem. Soc.*, 1967, **89**, 5065.

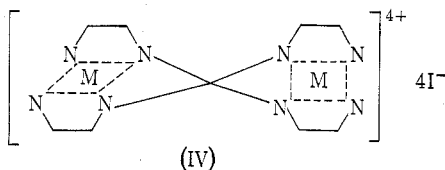
<sup>4</sup> Selbin, J., *J. inorg. nucl. Chem.*, 1961, **17**, 84.

<sup>5</sup> Sargeson, A. M., and Searle, G. H., *J. Am. chem. Soc.*, 1967, **89**, 787.

<sup>6</sup> Basolo, F., *J. Am. chem. Soc.*, 1948, **70**, 2634.

<sup>7</sup> Bailar, J. C., and Oehmke, R. W., *J. inorg. nucl. Chem.*, 1965, **27**, 2199.

( $\epsilon$  130), typical of the copper(II)-tetramine complexes.<sup>8,9</sup> The molar conductance in aqueous solution is 623 mho cm<sup>2</sup>, consistent with the value expected for a 4 : 1 electrolyte. There seems little doubt that the structure of this complex may be represented by (IV; M = Cu).



The palladium(II) complex of composition (Pd<sub>2</sub>LI<sub>4</sub>)2H<sub>2</sub>O was isolated as a yellow crystalline solid. Its molar conductance in aqueous solution was 520 mho cm<sup>2</sup> and structure (IV; M = Pd) is proposed for this complex.

In contrast to the above, the reaction between nickel(II) sulphate and the octamine (II) produced a pink solution, from which pale pink needles were isolated upon the addition of iodide ions. This complex was paramagnetic ( $\mu_{\text{eff}}$  2.3 B.M. at 23°) and showed visible absorption maxima at 465 nm ( $\epsilon$  7) and 523 nm ( $\epsilon$  9). These properties are not consistent with structure (IV; M = Ni), which would be diamagnetic and have a single absorption maximum in the visible spectrum at about 440 nm ( $\epsilon$  50–100), typical of the square-planar Ni-N<sub>4</sub> chromophore.<sup>10–12</sup> This complex has the composition (Ni<sub>2</sub>LI<sub>4</sub>)2H<sub>2</sub>O and it seems likely that one nickel ion is octahedrally coordinated to six nitrogen donors, while the other nickel ion is coordinated to two nitrogen donor atoms and two water molecules. The observed spectrum is similar to those reported for several Ni-N<sub>6</sub> chromophores.<sup>13</sup> A nickel(II) complex, containing a chelate structure similar to the moiety around the octahedral nickel ion of this complex, has been prepared<sup>14</sup> from a hexamine which has six amino groups arranged similarly to those in the octamine (II).

Structure (IV) is dissymmetric because of the inclination of the two planes containing the M-N<sub>4</sub> atomic units. We have attempted the resolution of (IV; M = Pd) by fractional crystallization of the (+)-antimonyl tartrate diastereoisomers, but we failed to obtain any optically active cations.

### Experimental

#### 6,6-Bis(2',5'-diazapentyl)-1,4,8,11-tetraazaundecane (II)

A solution of pentaerithrityl tetrabromide (40 g, 0.1 mole) dissolved in excess ethylenediamine (480 g, 8 mole) was heated under reflux for 50 hr. Excess ethylenediamine was recovered by distillation and the residual oil was made strongly alkaline with aqueous sodium hydroxide

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<sup>9</sup> Jørgensen, C. K., *Acta chem. scand.*, 1955, **9**, 1362.

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<sup>11</sup> Ballhausen, C. J., and Liehr, A. D., *J. Am. chem. Soc.*, 1959, **81**, 538.

<sup>12</sup> Glaser, H., and Pfeiffer, P., *J. prakt. Chem.*, 1939, **153**, 300.

<sup>13</sup> Manch, W., and Fernelius, W. C., *J. chem. Educ.*, 1961, **38**, 192.

<sup>14</sup> Green, R. W., Catchpole, K. W., Phillip, A. T., and Lions, F., *Inorg. Chem.*, 1963, **2**, 597.

(40 g in 100 ml). The mixture of amine products was extracted into pyridine ( $3 \times 200$  ml), which was separated from the aqueous layer and dried over potassium hydroxide pellets. After removal of pyridine and low-boiling amines, the mixture of amines having b.p.  $182-216^\circ/0.01$  mm was collected; yield 19.8 g. This mixture was redistilled and fractionated through a 15-cm unpacked column. The fraction having b.p.  $198-201^\circ/0.01$  mm,  $n_D^{32}$  1.5309, yield 4.9 g (15% of theoretical, based on the tetrabromide), was found to be the purest sample of the required *octamine*. This amine afforded an octakis-phenylthiourea derivative, m.p.  $135-138^\circ$  (Found: C, 59.8; H, 6.0.  $C_{69}H_{76}N_{18}S_8$  requires C, 59.8; H, 5.5%).

*6,6-Bis(2',5'-diazapentyl)-1,4,8,11-tetraazaundecanedicopper(II) Iodide*

An aqueous solution of copper(II) sulphate 5-hydrate (1.00 g, 4 mmole) was added to an aqueous solution of the octamine (0.61 g, 2 mmole). The resulting violet solution was stirred thoroughly and concentrated aqueous sodium iodide solution was added to it; violet needles of the *complex* separated. These crystals were recrystallized once from water containing sodium iodide; yield 0.85 g (Found: C, 16.9; H, 4.3; N, 11.4; Cu, 13.2.  $C_{13}H_{36}Cu_2I_4N_8$  requires C, 16.6; H, 3.9; N, 11.9; Cu, 13.5%).

*6,6-Bis(2',5'-diazapentyl)-1,4,8,11-tetraazaundecanedicupalladium(II) Iodide Dihydrate*

Potassium tetrachloropalladate(II) (0.82 g, 2.5 mmole) dissolved in water (5 ml) was added dropwise to a hot aqueous solution of the octamine (0.38 g, 1.25 mmole) over a period of 10 min. The resulting yellow solution was heated under reflux for 15 min, filtered, and poured into concentrated aqueous sodium iodide solution. Upon cooling, yellow needles of the *complex* precipitated and these were recrystallized from water containing sodium iodide; yield 0.45 g (Found: C, 14.8; H, 4.1; N, 9.6; Pd, 20.8.  $C_{13}H_{40}I_4N_8O_2Pd_2$  requires C, 14.7; H, 3.8; N, 10.6; Pd, 20.1%).

*Diaquo-6,6-bis(2',5'-diazapentyl)-1,4,8,11-tetraazaundecanedinickel(II) Diiodide*

To an aqueous solution of the octamine (0.61 g, 2 mmole) was added an aqueous solution of nickel(II) sulphate 6-hydrate (1.05 g, 4 mmole). Excess aqueous sodium iodide was added to the stirred pink solution and upon cooling, silky pink needles of the *complex* were obtained. The product was recrystallized from water containing sodium iodide (Found: C, 16.3; H, 4.5; N, 11.5; Ni, 12.6.  $C_{13}H_{40}I_4N_8Ni_2O_2$  requires C, 16.2; H, 4.1; N, 11.6; Ni, 12.2%).

*Acknowledgment*

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