

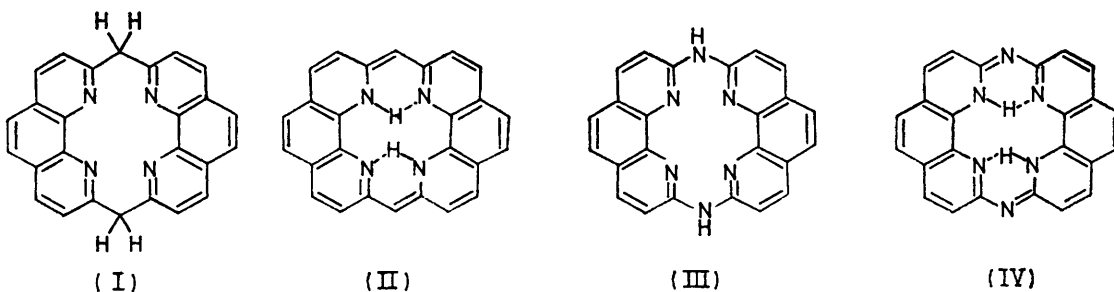
Preparation of a Conjugated Tautomer of 1,14:7,8-Diethenotetrapyrido-[2,1,6-de:2',1',6'-gh:2'',1'',6''-kl:2''',1''',6'''-na][1,3,5,8,10,12]hexa-azacyclotetradecine and its Metal Derivatives

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A hexa-aza-macrocyclic compound of high thermal stability is readily obtained from 2,9-diamino-1,10-phenanthroline by its thermolysis or by its condensation with 2,9-dihalogeno-1,10-phenanthroline. The structure of this macrocycle has been established as a conjugated system of a novel type, related to some extent to porphin and phthalocyanin. The macrocyclic compound forms copper, cobalt, and nickel complexes.

MANY cyclophane compounds have been prepared as they pose interesting theoretical and synthetic problems. Recently Haenel and Staab prepared some cyclophane compounds containing polynuclear aromatic rings, such

We now enlarge on our recent account² of the preparation of hexa-azaphenanthrenophane and also describe the synthesis of some metal derivatives. 2-Chloro-1,10-phenanthroline (V) prepared according to Halcrow



as phenanthrenophanes and naphthalenophanes.¹ We were interested in azacyclophane structures such as (I) and (III), because they may possibly tautomerize to the fully conjugated forms (II) and (IV) respectively.

¹ M. Haenel and H. A. Staab, *Tetrahedron Letters*, 1970, 3585.

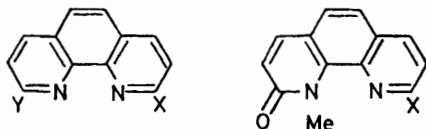
² S. Ogawa, T. Yamaguchi, and N. Gotoh, *J.C.S. Chem. Comm.*, 1972, 577.

and Kermack³ was oxidized with potassium ferricyanide and sodium hydroxide to afford 2-chloro-10-methyl-1,10-phenanthroline-9-one (VI). Treating (VI) with phosphorus pentachloride in phosphoryl chloride gave 2,9-dichloro-1,10-phenanthroline (VIII). In a

³ B. E. Halcrow and W. O. Kermack, *J. Chem. Soc.*, 1946, 156.

similar fashion, 2-bromo-9-chloro-1,10-phenanthroline (IX) and 2,9-dibromo-1,10-phenanthroline (X) were prepared from (VI) and 2-bromo-1,10-phenanthroline (VII) respectively. Ammonolysis of (VIII) in a mixture of phenol and acetamide by bubbling ammonia gas at 160° gave 2,9-diamino-1,10-phenanthroline (XI).

Compounds (VIII) and (XI) were heated in nitrobenzene in the presence of potassium carbonate as acid acceptor and gave a product which crystallized from quinoline to give yellow needles, m.p. 474° (decomp.). The yield of the product was slightly improved when (IX) or (X) was used instead of (VIII).

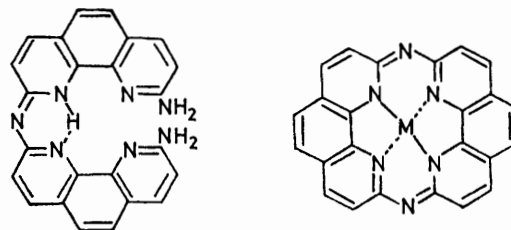


- | | |
|--------------------------|------------|
| (V) X=H, Y=Cl | (VI) X=Cl |
| (VII) X=H, Y=Br | (VII) X=Br |
| (VIII) X=Y=Cl | |
| (IX) X=Cl, Y=Br | |
| (X) X=Y=Br | |
| (XI) X=Y=NH ₂ | |

The cyclic structure of the product is well supported by spectral evidence. This compound is capable of existing in the tautomeric forms (III) and (IV). Although its existence as either (III) or (IV) in solution is not clearly indicated by its n.m.r. or i.r. spectrum (limited solubility in neutral organic solvents), its solid state i.r. spectrum (KBr disc or Nujol mull) shows that the solid exists in form (IV). It shows ν_{\max} 2780 cm^{-1} , and since this band falls to 2130 cm^{-1} upon deuteration of the inner NH protons, it is assigned to the N-H stretching vibration (ν_{NH}). The ν_{NH} of this compound is much lower than those of porphyrin (3324 cm^{-1})⁴ and phthalocyanin (3200 cm^{-1}).⁵ This result is explained in terms of the very strong intramolecular N-H...N bridges in the former. The macrocycle (IV) was also obtained almost quantitatively by thermolysis of (XI) at 280–300°. The yellow needles obtained were identical with the material prepared by condensation of (VIII) and (XI). Formation of the macrocycle by this reaction proceeds remarkably easily and (XI) shows no tendency to lead to linear polycondensation products. A reasonable explanation seems to be that the intermediate (XIII) can assume a configuration favourable to cyclisation by formation of an intramolecular N-H...N bridge.

When 2,9-dihalo-1,10-phenanthroline and (XI) were heated in the presence of metal salts and potassium carbonate, the yellow-brown copper complex (XIV; M = Cu), the yellow nickel complex (XIV; M = Ni), and the red-brown cobalt complex (XIV; M = Co) were obtained. The structures were supported by

mass spectra; m/e 449/447 for (XIV; M = Cu), m/e 444/442 for (XIV; M = Ni), and m/e 443 for (XIV; M = Co). These parent peaks were very intense, and



(XIII)

(XIV)

relatively strong doubly charged ion spectra were observed in all cases. As in the case of the metal-free macrocycle (IV), the M^+ and M^{2+} peaks were much more intense than those of the fragment ions. The thermal stability of the metal complexes was determined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) methods. The DTA curves in air showed no exotherms below 400°, but strong decomposition exotherms with weight loss in TGA at 418° for (XIV; M = Cu), at 412° and 460° for (XIV; M = Ni), and at 420° for (XIV; M = Co). The copper and cobalt complexes are paramagnetic, giving only very broad n.m.r. signals in trifluoroacetic acid (TFA). The nickel complex is diamagnetic and its n.m.r. spectrum is well resolved in TFA: $\delta(\text{TFA})$ 9.08 (d, 4-H), 8.39 (s, 5-H), and 8.23 (d, 3-H). Metal complexes were also obtained in good yields by treatment of a hot nitrobenzene solution of the metal-free macrocycle (IV) with cupric, nickel, and cobalt acetates in benzyl alcohol.

EXPERIMENTAL

I.r. spectra were measured for potassium bromide discs or Nujol mulls with a Hitachi-Perkin-Elmer 125 spectrophotometer. N.m.r. spectra were determined for trifluoroacetic acid solutions with a Hitachi R-20A 60 MHz instrument with tetramethylsilane as internal reference. Mass spectra were obtained by direct insertion into the ion source of a Hitachi RMU-6D instrument.

2-Chloro-10-methyl-1,10-phenanthroline-9-one (VI).—A mixture of 2-chloro-1,10-phenanthroline (V) (15.9 g) and dimethyl sulphate (50 ml) was maintained at 120° for 1 h. After cooling, the mixture was poured into dry ether (300 ml) with stirring. The white precipitate (20.1 g), which was very hygroscopic and was used without further purification, crystallized from ethanol as needles, m.p. 208°. To an ice-cooled solution of potassium ferricyanide (53 g) in water (150 ml) were added alternately in small portions a solution of sodium hydroxide (80 g) in water (300 ml) and a solution of the foregoing white solid in water (300 ml). The pale yellow precipitate was refluxed with benzene, and the solution on removal of benzene yielded needles of (VI) (12.9 g, 77.2%), m.p. 153–154° (Found: C, 64.0; H, 3.6; N, 11.5. $\text{C}_{13}\text{H}_9\text{ClN}_2\text{O}$ requires C, 63.8; H, 3.7; N, 11.5%).

2,9-Dichloro-1,10-phenanthroline (VIII).—The chloroketone (VI) (2.0 g), phosphorus pentachloride (2.5 g), and

⁴ G. M. Badger, R. L. N. Harris, R. A. Jones, and J. M. Sasse, *J. Chem. Soc.*, 1962, 4329.

⁵ T. Kobayashi, F. Kurokawa, N. Uyeda, and E. Suito, *Spectrochim. Acta*, 1970, 26A, 1305.

phosphoryl chloride (15 ml) were refluxed for 8 h. After removal of excess of phosphoryl chloride by distillation under reduced pressure, iced water (100 g) was added and the solution basified with ammonia. The precipitate crystallized from benzene as *needles* of (VIII) (1.93 g, 95%), m.p. 249—250° (Found: C, 57.5; H, 2.3; N, 11.3. $C_{12}H_6Cl_2N_2$ requires C, 57.9; H, 2.4; N, 11.3%).

2-Bromo-1,10-phenanthroline (VII).—10-Methyl-1,10-phenanthroline-9-one (1 g), phosphorus pentabromide (2.5 g), and phosphoryl bromide (6.5 g) were heated at 80° for 6 h in an atmosphere of nitrogen. After cooling, the mixture was poured into iced water and the solution basified with ammonia. The precipitate crystallized from benzene as *needles* of (VII) (1.04 g, 84.6%), m.p. 164—165° (Found: C, 55.5; H, 2.5; N, 10.8. $C_{12}H_7BrN_2$ requires C, 55.6; H, 2.7; N, 10.8%).

2-Bromo-10-methyl-1,10-phenanthroline-9-one (XII).—In a similar manner to the synthesis of (VI), the *ketone* (XII), m.p. 154—155°, was obtained in 93% yield from potassium ferricyanide (5.5 g) in water (30 ml), sodium hydroxide (17 g) in water (50 ml), and 2-bromo-1,10-phenanthroline methiodide (m.p. 228—229°) (2.03 g; prepared by a modification of Halcrow and Kermack's procedure³) in water (500 ml) (Found: C, 54.3; H, 3.2; N, 9.6. $C_{13}H_9BrN_2O$ requires C, 54.0; H, 3.0; N, 9.7%).

2-Bromo-9-chloro-1,10-phenanthroline (IX).—The *ketone* (VI) (2.1 g), phosphorus pentabromide (5 g), and phosphoryl bromide (20 g) were heated at 80° for 5 h in an atmosphere of nitrogen. Treatment of the mixture with iced water and ammonia gave (IX) as *plates* (2.4 g, 98.6%), m.p. 251—252.5° (from benzene) (Found: C, 48.8; H, 1.9; N, 9.3. $C_{12}H_6BrClN_2$ requires C, 49.1; H, 2.1; N, 9.5%).

2,9-Dibromo-1,10-phenanthroline (X).—In a similar manner to the synthesis of (IX), (X) was obtained in 96.7% yield from (XII) as pale yellow *plates*, m.p. 248—249° (Found: C, 42.4; H, 1.7; N, 8.3. $C_{12}H_6Br_2N_2$ requires C, 42.6; H, 1.8; N, 8.3%).

2,9-Diamino-1,10-phenanthroline (XI).—A stream of ammonia gas was bubbled through a solution of (VIII) (2.0 g) in a mixture of phenol (10 g) and acetamide (3.5 g), maintained at 160° for 8 h. The phenol and acetamide were removed by distillation under reduced pressure and the residue was dissolved in acetic acid (10 ml). 4N-Sodium hydroxide was added until the mixture was alkaline. The precipitated (XI) (1.37 g, 81.2%) crystallized from ethanol in pale yellow *prisms*, m.p. 273—275° (Found: C, 68.1; H, 4.6; N, 26.3. $C_{12}H_{10}N_4$ requires C, 68.6; H, 4.8; N, 26.7%).

Hexa-aza-macrocycle (IV).—(a) A mixture of (VIII) (125 mg), (XI) (105 mg), potassium carbonate (138 mg), and nitrobenzene (10 ml) was maintained at 180° with stirring for 5 h. Yellow *needles* separated. The mixture was steam-distilled to remove nitrobenzene, the residue on

filtration giving yellow *needles* of substantially pure 3bH,10bH-1,14:7,8-diethenotetrapyrido[2,1,6-de:2',1',6'-gh:2'',1'',6''-kl:2''',1''',6'''-na][1,3,5,8,10,12]hexa-azacyclo-tetradecine (IV) (182 mg, 94%). Recrystallization from quinoline afforded yellow *needles* (112 mg) (Found: C, 75.0; H, 3.3; N, 21.7. $C_{24}H_{14}N_6$ requires C, 74.6; H, 3.7; N, 21.8%).

(b) Compound (XI) was heated in an atmosphere of nitrogen. Yellow *needles* separated at 280° by evolution of ammonia. After solidification was completed, heating was continued at 300° for 1 h. The product was washed with chloroform and the yellow *needles* obtained were identical with those prepared in (a).

Hexa-aza-macrocycle-Metal Complexes.—(a) **Copper complex** (XIV; M = Cu). To a mixture of (VIII) (125 mg), (XI) (105 mg), anhydrous potassium carbonate (140 mg), and nitrobenzene (10 ml) maintained at 180° was added anhydrous copper(II) chloride (90 mg) with stirring in an atmosphere of nitrogen and the mixture was stirred at 180° for 5 h. The mixture was steam-distilled to remove nitrobenzene, the residue on filtration giving brownish yellow *needles* of substantially pure copper hexa-aza-macrocycle (XIV; M = Cu) (212 mg, 94%). Recrystallization from quinoline afforded brownish yellow *needles* (Found: C, 64.2; H, 2.5; N, 19.0. $C_{24}H_{12}CuN_6$ requires C, 64.4; H, 2.7; N, 18.8%).

Nickel complex (XIV; M = Ni). A mixture of (VIII) (125 mg), (XI) (105 mg), nickel(II) acetate hydrate (178 mg), potassium carbonate (206 mg), and nitrobenzene (10 ml) was maintained at 170° with stirring for 3 h. Yellow *needles* separated and were washed with nitrobenzene, acetone, and water, and dried, giving yellow *needles* of substantially pure *nickel complex* (XIV; M = Ni) (191 mg, 86%) (Found: C, 65.3; H, 2.5; N, 18.6. $C_{24}H_{12}N_6Ni$ requires C, 65.1; H, 2.8; N, 18.4%).

Cobalt complex (XIV; M = Co). A mixture of (VIII) (125 mg), (XI) (105 mg), cobalt(II) acetate tetrahydrate (162 mg), potassium carbonate (206 mg), and nitrobenzene (10 ml) was maintained at 170° with stirring for 3 h. Brown *needles* separated and were washed with nitrobenzene, acetone, and water, and dried, giving brown *needles* of substantially pure *cobalt complex* (XIV; M = Co) (174 mg, 78.3%), which for analysis was crystallized from quinoline (Found: C, 64.8; H, 3.1; N, 18.3. $C_{24}H_{12}CoN_6$ requires C, 65.0; H, 2.7; N, 18.4%).

(b) The macrocycle (IV) was dissolved in nitrobenzene by heating under reflux, and a solution of the appropriate metal acetate hydrate in hot benzyl alcohol was added. The metal hexa-aza-macrocycle immediately crystallized and was collected after 5 min. The products were identical with those obtained from preparation (a).