An Intermediate for the Synthesis of Cyclic Tetramine Ligands: 4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11-dione

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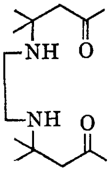
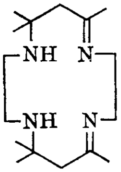
THE β-amino-ketone, 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione, (β), has been isolated as a dihydroperchlorate salt, β,$2HClO_4$. The amino-ketone is a useful intermediate for the synthesis of cyclic tetramine ligands. By use of β,$2HClO_4$ the following new copper(II) and nickel(II) complexes have been synthesised as perchlorate salts.

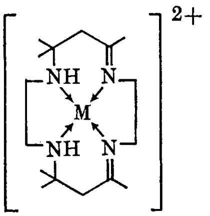

(β)

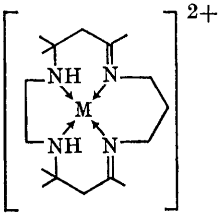

(B)

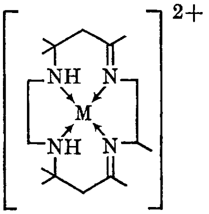
The complexes were prepared in 20—50% yield by condensation of β with the appropriate diamine (or ammonia) in the presence of the metal ion in methanol or aqueous solution. The reaction stoicheiometries employed were β,$2HClO_4$ + 2(diamine) + metal perchlorate (or metal–bisdiamine complex or metal–ammine complex) or β,$2HClO_4$ + MCO_3 + diamine.

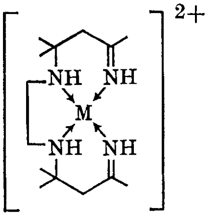
The *cis*-diene configuration for the complexes was confirmed by removal of the metal ion (cyanide[1]) and decomposition of the ligand in perchloric acid to give β,$2HClO_4$. The nickel complexes have magnetic properties and visible absorption spectra characteristic of four co-ordinate square-planar diamagnetic nickel(II). The complexes with cyclic ligands, (I)—(IV), show considerable stability toward the specific metal-ion reagents α-benzoin oxime (copper) and dimethylglyoxime (nickel). All the complexes are decomposed by aqueous cyanide and the complexes (II), (III), (V), and (VI) are decomposed by dilute hydrohalic acids. Characteristic infrared absorptions are observed for the groupings $>C=N$ (1660 ± 5 cm.$^{-1}$), $>NH$ (3210—3180 cm.$^{-1}$) and, in (V) and (VI), for $>NH$ (3265 cm.$^{-1}$). (I) is identical to the complex obtained from $NiB(ClO_4)_2$ by ligand transfer;[1] the *trans*-diene isomer $CuA(ClO_4)_2$ has been reported.[2] Curtis and House[3] have reported the *trans*-diene analogue of (III) and the *trans* configuration has now been confirmed by *X*-ray and infrared comparisons with complex (III).

The synthesis of β,$2HClO_4$ commences with the complex 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,14-dienenickel(II) perchlorate, $NiB(ClO_4)_2$, which is a product of the reaction of trisdiaminoethanenickel(II) perchlorate with acetone.[4] The ligand B can be obtained in non-aqueous solution after removing the metal ion from the complex and precipitating it as $K_2Ni(CN)_4$.[1] By use of the ligand solution the complexes $CuB(ClO_4)_2$, $ZnBZnCl_4,CH_3OH$, and $FeBCl_2FeCl_4,H_2O$ have been prepared,[5] and also a series of dimeric cobalt(II) complexes which are thought to contain the unit Y–CoB–CoB–Y.[1] Reaction of the iron(III) or zinc(II) complex with dilute perchloric acid, or addition of a methanolic solution [1] of B to dilute perchloric acid gives the dihydroperchlorate salt of 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione, (β), yield 80%. The salt is sparingly soluble in water and the lower alcohols.


(I) M=Cu (orange)


(II) M=Cu (mauve)
(III) M=Ni (orange)


(IV) M=Cu (orange)


(V) M=Cu (mauve)
(VI) M=Ni (yellow)

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[1] J. L. Love and H. K. J. Powell, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 113.

[2] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 3011.

[3] N. F. Curtis and D. A. House, *J. Chem. Soc.* (*A*), 1967, 537.

[4] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.* (*A*), 1966, 1015.

[5] J. L. Love and H. K. J. Powell, unpublished results.