Preparation and Transmetallation of a Neutral Magnesium(II) Complex of a Tetra-aza Macrocyclic Ligand: *X*-Ray Structure of {17,18,19,20-Tetrahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetra-azacyclotetradecinato(2−)}oxovanadium(IV)

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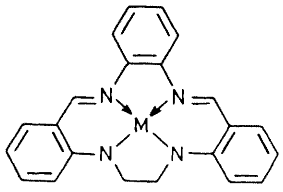
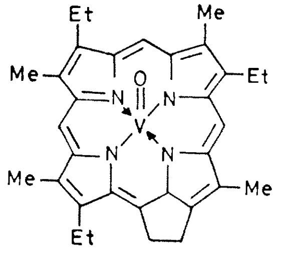
Summary A neutral magnesium(II) complex has been obtained from reactions of a planar conjugated 'N_4' macrocyclic ligand (**1**) with Grignard reagents, it readily undergoes a transmetallation reaction to give a neutral square-pyramidal oxo-vanadium(IV) complex, the structure of which has been determined by *X*-ray crystallography

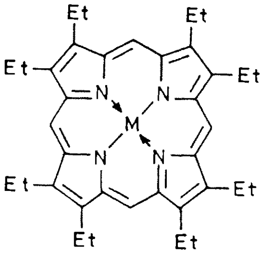
Although Fe, Co, Ni and Cu complexes of 17,18,19,20-tetrahydrotribenzo[*e*,*i*,*m*][1,4,8,11]tetra-azacyclotetradecine (**1**) have been characterized,[1] attempts to prepare a magnesium(II) complex by similar routes [*e g* (**1**) + $Mg(MeCO_2)_2$ or $Mg(ClO_4)_2$–pyridine] failed This magnesium complex would be of interest because it would allow comparisons with naturally occurring chlorophylls, and because structural comparisons with the free ligand and transition metal complexes[2] may allow assessments to be made of the importance of intramolecular H-bonding and metal *d* orbital participation in changes of ligand conformation and geometry



(1) M = H
(2) M = Mg
(3) M = VO
(6) M = Ni



(5)



(4) M = VO
(7) M = Mg(py)$_2$

We report here that the neutral magnesium(II) complex (**2**) may be obtained from the reaction of a Grignard reagent (PhMgBr, EtMgBr, or EtMgI) with the free ligand (**1**) in a 2 : 1 molar ratio in diethyl ether The red, ether-insoluble complex (**2**) is hydrolytically unstable, and regenerates the free ligand (**1**) on treatment with water Addition of further quantities of ethereal Grignard reagent to solid (**2**) results in dissolution to give a red solution from which the free ligand (**1**) cannot be recovered after treatment with water It is assumed that this further reaction involves alkylation at the azomethine carbon atom,[3] although no attempt has yet been made to characterize the products

The ready replacement of Mg^{2+} from (**2**) by Lewis acids other than protons, for instance by transition metal dications, may yield complexes which are difficult to prepare directly from (**1**) For example, a suspension of (**2**) in Et$_2$O–CH$_2$Cl$_2$ (1 : 1) when shaken with a slight excess of VO(acac)$_2$ at room temperature, gives the vanadyl complex (**3**) (Hacac = acetylacetone), the structure of which has been determined by *X*-ray crystallography † Reactions of the free ligand (**1**) with VO(acac)$_2$ in a variety of solvents failed to yield (**3**) Other workers[4] have used transmetallation as a route to otherwise inaccessible metal macrocyclic complexes

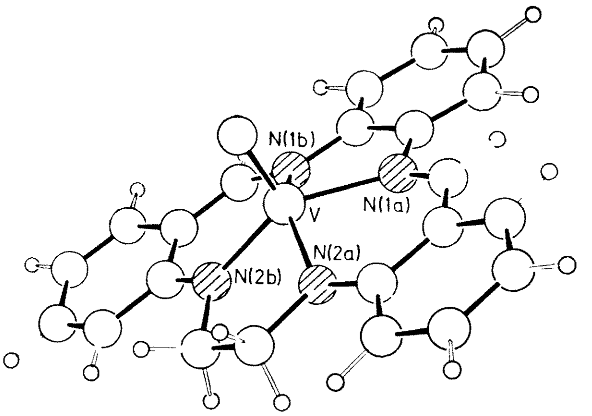


FIGURE The structure of the vanadyl complex (**3**) Bond lengths to the V atom are O 1 61(1), N(1a) 2 03(1), N(1b) 2 07(1), N(2a) 1·99(1), and N(2b) 1 97(1) Å Bond angles (mean e s d 0 6°) defined by pairs of donors at the V atom are O N(1a) 108 0, O,N(1b) 105 6, O N(2a) 109 5, O N(2b) 109 7, N(1a),N(1b) 79 6, N(1a),N(2a) 87 1, N(1a),N(2b) 142 1, N(1b), N(2a) 144 7, N(1b),N(2b) 87 4, and N(2a),N(2b) 83·3°

The vanadyl complex (**3**) has an approximately square-pyramidal structure (Figure) similar to that[5] in (**4**) and in the petroporphyrin (**5**) The displacement of the V atom from the best 'N$_4$' plane in (**3**) (0 63 Å) is greater than in the porphyrin complexes (**4**) and (**5**) (0 48 and 0·54 Å), while the mean V–N bond length is shorter These observations are to be expected since the dianion of the 14-membered ring (**1**) should have a smaller 'hole size' than the 16-membered porphyrin dianions

A feature of interest is the co-ordination geometry shown by the Mg atom in (**2**) A co-ordination number of 5 and the displacement of the Mg atom from the 'N$_4$' plane have been observed in several chlorophyll and magnesium porphyrin structures which contain an axial water molecule For (**2**), analytical data exclude the presence of an additional ligand, and the similarity of the i r spectrum to that of the Ni^{II} complex (**6**) suggests a similar structure The magnesium would then lie close to the 'N$_4$' plane, possibly with intermolecular contacts allowing achievement of an effective co-ordination number of 5 or 6 An 'in plane' structure for a magnesium porphyrin (**7**) has been reported recently,[6] though in that case the magnesium is six-co-ordinated

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† *Crystal data* $C_{22}H_{18}N_4OV$, red needles from dimethylformamide, $M = 405\ 4$, monoclinic, space group $P2_1/c$, $a = 15\ 387$, $b = 13{\cdot}918$, $c = 8\ 253$ Å, $\beta = 94\ 06°$, $Z = 4$, $I/\sigma(I) \geqslant 3\ 0$, θ-range 3—20°, $R = 0\ 085$ for 995 reflections obtained on a Philips PW1100 diffractometer with Mo-K_α radiation

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1WE Any request should be accompanied by the full literature citation for this communication

[1] M Green and P A Tasker, *Inorg Chim Acta*, 1971, **5**, 65, P G Owston and P A Tasker, unpublished results

[2] P G Owston, R Peters, and P A Tasker, American Chemical Society Meeting, Hawaii, April 1979 INOR 298, J Trotter, unpublished work

[3] G Tennant, in 'Comprehensive Organic Chemistry,' vol 2 ed I O Sutherland, Pergamon, 1979, p 410

[4] C Cairns, S G McFall, S M Nelson, and M G B Drew, *J C S Dalton*, 1979, 446

[5] F S Molinaro and J A Ibers, *Inorg Chem* , 1976, **15**, 2278, R C Petterson, *Acta Cryst* , 1969, **B25**, 2527

[6] R Bonnett, M B Hursthouse, K M A Malik, and B Mateen, *J C S Perkin II*, 1977, 2072