Five-co-ordinate Magnesium Complexes: Synthesis and Structure† of Quadridentate Schiff-base Derivatives

Fabio Corazza and Carlo Floriani *
Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1005 Lausanne, Switzerland
Angiola Chiesi-Villa and Carlo Guastini
Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy
S. Ciurli (in part)
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, I-56100 Pisa, Italy

Reaction of dibenzylmagnesium in tetrahydrofuran (thf) with the quadridentate Schiff-base ligands *NN'*-ethylenebis(acetylacetoneimine) (H_2acen), *NN'*-ethylenebis(salicylideneimine) (H_2salen), *NN'*-*o*-phenylenebis(salicylideneimine) (H_2salphen), or 7,16-2*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetra-azacyclotetradecine (H_2tmdbtd) afforded in a good yield the corresponding magnesium complexes [{Mg(acen)}$_2$] (**1**), [{Mg(salen)}$_2$] (**2**), [{Mg(salphen)}$_2$] (**3**), and [Mg(tmdbtd)(thf)] (**4**). The dimeric nature of the Schiff-base complexes (**1**)—(**3**), which was proven by an *X*-ray analysis on complex (**1**), allows magnesium five-co-ordination. The acidity of a four-co-ordinate magnesium in complex (**4**) is shown by the formation of a very stable adduct with thf. The structure of (**4**) has also been determined by *X*-ray analysis. Complex (**1**): space group $P2_1/c$ (monoclinic), a = 10.825(2), b = 11.845(3), c = 10.734(3) Å, β = 92.80(2)°, Z = 2, R = 0.050 for 957 observed reflections. Complex (**4**): space group *Cmcm* (orthorhombic), a = 14.212(2), b = 8.306(1), c = 19.350(4) Å, Z = 4, R = 0.042 for 900 observed reflections.

There is surprisingly little reported on the co-ordination chemistry of magnesium bonded to polydentate or macrocyclic ligands.[1] The central role of magnesium in chlorophyll[2] has not promoted synthetic and reactivity studies on magnesium co-ordination compounds; only porphyrin complexes have been relatively well studied.[1-3] We identify three areas of major interest in magnesium co-ordination chemistry: (i) studies on redox properties of magnesium complexes and the reactivity of their reduced or oxidized forms (since magnesium itself cannot be involved in redox processes, this study will be mainly centred on the chemistry of the ligand bonded to magnesium);[4] (ii) studies on Lewis acidity of four-co-ordinate magnesium in the presence of oxygen donor ligands;[3-5] (iii) the search for a relationship between the chemistry of simple magnesium complexes and naturally occurring systems.

A crucial problem for producing neutral complexes of magnesium is the synthetic methodology. Synthesis from magnesium salts either in organic or aqueous solutions have limited success because of the hydrolysability and oxophilicity of magnesium.[1,6] Synthesis from $Mg(ClO_4)_2$ in pyridine or dimethylformamide requires strongly co-ordinating ligands like porphyrins.[7] Analogous reactions with other magnesium salts led to the corresponding adducts.[1,6] Dialkylmagnesium derivatives can be used for reactions with ligands having active protons; however, this is limited to those which do not contain functionalities reacting with magnesium alkyls. In spite of the well known reactivity of Grignard reagents with imino groups,[8] we found the reaction of $Mg(CH_2Ph)_2$ an excellent method for binding magnesium to quadridentate Schiff-base and 14-membered tetramethyltetra-aza-macrocyclic ligands. We report here a series of neutral five-co-ordinate magnesium complexes containing quadridentate ligands.

Experimental

All the reactions were carried out under an atmosphere of dry and purified nitrogen, because of the very high sensitivity of complexes to hydrolysis. Schiff-base ligands were prepared by conventional condensation of salicylaldehyde or acetylacetone with the corresponding diamine in EtOH or benzene. The synthesis of H_2tmdbtd‡ was performed as reported in the literature.[9] Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer and ^{1}H n.m.r. using a WP-300 Bruker instrument.

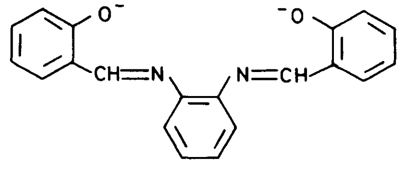
Synthesis of [{Mg(acen)}$_2$] (**1**).—A tetrahydrofuran (thf) solution of $Mg(CH_2Ph)_2$ (70 cm^3, 0.205 mol dm^{-3}) was slowly added to a thf solution (50 cm^3) of H_2acen (3.20 g, 14.3 mmol). The yellow fluorescent solution was evaporated to dryness. The solid residue was dissolved in boiling toluene (60 cm^3). The toluene solution, on cooling and standing at room temperature for 2 d, gave yellow crystals of (**1**) (yield *ca.* 60%) (Found: C, 58.70; H, 7.35; N, 11.40. Calc. for $C_{24}H_{36}Mg_2N_4O_4$: C, 58.45; H, 7.30; N, 11.35%); ν(C=N) (Nujol), 1 610 cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$], δ 4.89 (s, 2 H), 3.12 (m, 2 H), 2.88 (m, 2 H), 1.98 (s, 6 H), and 1.51 (s, 6 H).

Synthesis of [{Mg(salen)}$_2$] (**2**).—A thf solution of $Mg(CH_2Ph)_2$ (60 cm^3, 0.20 mol dm^{-3}) was slowly added to a thf solution (50 cm^3) of H_2salen (3.2 g, 11.94 mmol). The yellow solution gave on standing at room temperature for 24 h yellow crystals of (**2**) (yield *ca.* 60—65%) (Found: C, 66.55; H, 4.70; N, 9.15. Calc. for $C_{32}H_{28}Mg_2N_4O_4$: C, 66.40; H, 4.85; N, 9.65%); ν(C=N) (Nujol), 1 650 and 1 625 cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$], δ

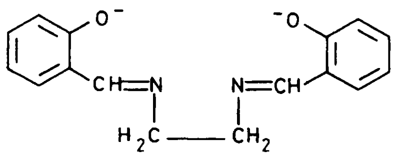
---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

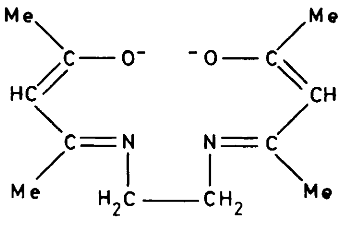
‡ Ligand abbreviations: H_2salphen = *o*-phenylenebis(salicylideneimine), H_2salen = *NN'*-ethylenebis(salicylideneimine), H_2acen = *NN'*-ethylenebis(acetylacetonimine), H_2tmdbtd = 7,16-2*H*-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine.



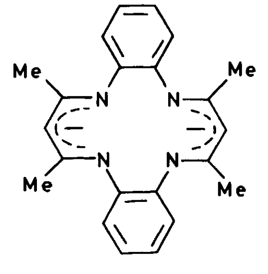
salphen



salen



acen



tmdbtd

Table 1. Experimental data for the *X*-ray diffraction studies on complexes (**1**) and (**4**)

Complex	(1)	(4)
Formula	$C_{24}H_{36}Mg_2N_4O_4$	$C_{26}H_{30}MgN_4O$
M	493.2	438.9
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (C^5_{2h}, no. 14)	*Cmcm* (D^{17}_{2h}, no. 63)
Cell parameters[a]		
a/Å	10.825(2)	14.212(2)
b/Å	11.845(3)	8.306(1)
c/Å	10.734(3)	19.350(4)
α/°	90	90
β/°	92.80(2)	90
γ/°	90	90
U/Å^3	1 374.7(6)	2 284.2(6)
Z	2	4
D_c/g cm^{-3}	1.192	1.276
Crystal dimensions (mm)	0.16 × 0.42 × 0.55	0.20 × 0.30 × 0.60
Linear absorption coefficient (cm^{-1})	1.16	8.43
Diffractometer	Philips PW 1100	Siemens AED
Diffraction geometry	equatorial	equatorial
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan speed (°/min)	6	3—12
Scan width (°)	1.20	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$[b]
Radiation (λ/Å)	Graphite-monochromated Mo-K_α (0.7107)	Nickel-filtered Cu-K_α (1.5418)
2θ range (°)	6—47	6—140
Reflections measured	$\pm h, \pm k, l$	$\pm h, \pm k, l$
Total data measured	3 939	4 021
Total unique data	2 029	1 215
Criterion for observation	$I > 3\sigma(I)$	$I > 2\sigma(I)$
Unique observed data	957	900
Agreement factor[c]	0.049	0.026
No. of variables	154	81
Overdetermination ratio	6.2	11.1
Max. shift/error on last cycle	0.1	0.2
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.050	0.042
$R' = \Sigma w^{\frac{1}{2}}\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$		0.048
G.o.f. $= [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_o - N_v)]^{\frac{1}{2}}$[d]		1.85

[a] Unit-cell parameters were obtained at 295 K by least-squares analysis of the setting angles of 35 carefully centred reflections chosen from diverse regions of reciprocal space. [b] $\Delta\theta = [(\lambda_{\alpha 2} - \lambda_{\alpha 1})/\lambda]\tan\theta$. [c] Between equivalent reflections. [d] G.o.f. = goodness of fit; N_o and N_v = numbers of observations and variables.

10.10 (s, 2 H), 7.81 (d, 2 H), 7.62 (t, 2 H), 7.10 (m, 4 H), and 4.32 (s, 2 H).

The synthesis of [{Mg(salphen)}$_2$] (**3**) was carried out following the same procedure (Found: C, 69.85; H, 4.10; N, 8.30. Calc. for $C_{40}H_{28}Mg_2N_4O_4$: C, 70.95; H, 4.15; N, 8.30%); ν(C=N) (Nujol), 1 610 cm^{-1}; ^{1}H n.m.r. [(CD$_3$)$_2$CO], δ 9.90 (s, 2 H), and 7.80—6.20 (m, 12 H).

Synthesis of [Mg(tmdbtd)(thf)].—A thf solution of Mg(CH$_2$Ph)$_2$ (23.3 cm^3, 0.50 mol dm^{-3}) was added to a suspension of H$_2$tmdbtd (4.0 g, 11.6 mmol) in thf (100 cm^3). The resulting red solution was left to stand at room temperature for 24 h. A red-orange crystalline solid formed (yield 3.35 g, 66%) (Found: C, 73.35; H, 6.75; N, 12.20. Calc. for $C_{26}H_{30}MgN_4O$: C, 71.15; H, 6.90; N, 12.75%); ^{1}H n.m.r. (CDCl$_3$), δ 1.54 (m, 4 H), 2.19 (s, 12 H), 3.38 (m, 4 H), 4.65 (s, 4 H), and 6.95 (m, 4 H).

Determination of the Structures.—Crystal data for complexes (**1**) and (**4**) are listed in Table 1. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. The reduced cells quoted were obtained with use of TRACER.[10] For intensities and background the 'three-point' technique was used for complex (**1**), while individual reflection profiles were analysed for (**4**).[11] The structure amplitudes were obtained after the usual Lorentz and polarization corrections * and the absolute scale was established by the Wilson method.[13] The crystal quality was tested by ψ

---

* Data reduction, structure solution and refinement were carried out on a Gould 32/77 computer using SHELX 76.[12]

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for complex (**1**)

Atom	*X/a*	*Y/b*	*Z/c*
Mg	3 597(2)	−91(2)	13(2)
O(1)	4 930(4)	1 111(3)	170(4)
O(2)	2 901(4)	220(4)	−1 664(4)
N(1)	3 062(5)	454(4)	1 794(5)
N(2)	2 060(4)	−1 129(4)	317(5)
C(1)	5 675(6)	3 007(6)	371(7)
C(2)	4 858(5)	2 069(5)	806(6)
C(3)	4 116(6)	2 240(5)	1 758(6)
C(4)	3 268(6)	1 453(6)	2 279(6)
C(5)	2 614(7)	1 863(7)	3 399(7)
C(6)	2 140(6)	−278(7)	2 353(6)
C(7)	2 053(7)	−1 389(6)	1 647(7)
C(8)	−12(8)	−1 962(7)	−89(9)
C(9)	1 151(6)	−1 333(5)	−472(7)
C(10)	1 144(6)	−975(6)	−1 748(7)
C(11)	1 983(6)	−256(5)	−2 250(6)
C(12)	1 842(8)	43(7)	−3 621(7)

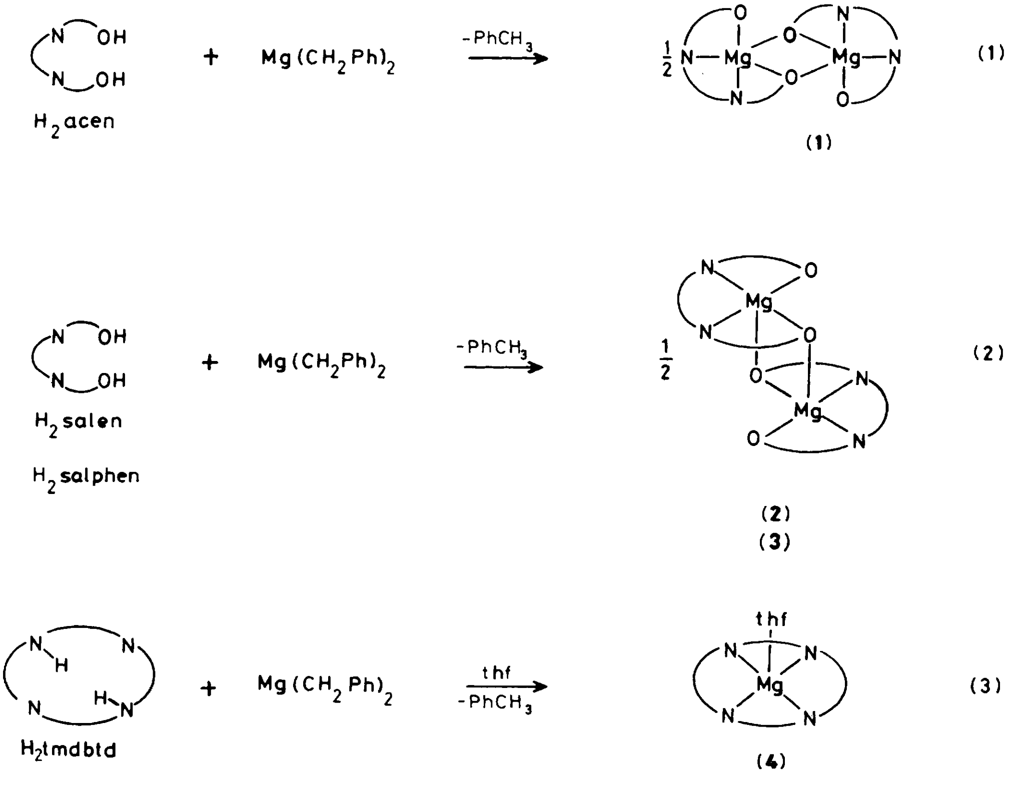
scans showing that crystal absorption effects could be neglected for complex (**4**), but not for complex (**1**), so the data for the latter were corrected for absorption following a semiempirical method.[14] The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. The final difference maps showed no usual feature, with no peak above the general background. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. At the end of refinement the values for k and g were 2.0256 and 0.000 71 respectively for complex (**4**); unit weights were used for complex (**1**). Anomalous scattering corrections were included in all structure factor calculations.[15b] Scattering factors for neutral atoms were taken from ref. 15*a* for non-hydrogen and from ref. 16 for H. Among the low-angle reflections, no correction for secondary extinction was deemed necessary. Solution and refinement were based on the observed reflections (Table 1).

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for complex (**4**)

Atom	*X/a*	*Y/b*	*Z/c*
Mg	0	2 243(1)	2 500
O(1)	0	4 700(3)	2 500
N(1)	929(1)	1 563(2)	1 737(1)
C(1)	502(1)	1 854(2)	1 089(1)
C(2)	979(1)	2 308(2)	487(1)
C(3)	487(2)	2 733(3)	−109(1)
C(4)	1 712(1)	712(2)	1 838(1)
C(5)	2 082(2)	394(3)	2 500
C(6)	2 231(2)	−102(3)	1 247(1)
C(7)	0	5 697(4)	1 900(2)
C(8)	0	7 337(4)	2 125(2)

For compound (**1**) the magnesium atom position was found from a three-dimensional Patterson map; the remaining non-hydrogen atoms were located in successive Fourier syntheses. Refinement was first carried out isotropically, then anisotropically for all non-hydrogen atoms using full-matrix least-squares methods. The hydrogen atoms were located in a difference Fourier synthesis and included in the subsequent calculations as fixed contributors ($U_{iso} = 0.10$ Å^2). Final co-ordinates for the non-hydrogen atoms are given in Table 2.

For compound (**4**) the systematic absences were consistent with the space groups *Cmcm*, *Ama*2, and *Cmc*2. *E*-Statistics, calculated as a function of sinθ, favoured the centrosymmetric *Cmcm*, $\langle|E^2 - 1|\rangle$ being 0.92. The structure was then solved in that space group starting from a three-dimensional Patterson map that indicated the magnesium atom to lie on the intersection of two mirror planes. Refinement was carried out as above. The molecule possesses an imposed crystallographic *mm* symmetry which requires the thf molecule to lie on and to be bisected by the mirror planes. Refinement resulted in rather high U_{ij} values for two independent carbons of thf, suggesting the possibility of the space group being the non-centrosymmetric *Ama*2 (where the mirror plane containing thf is released).



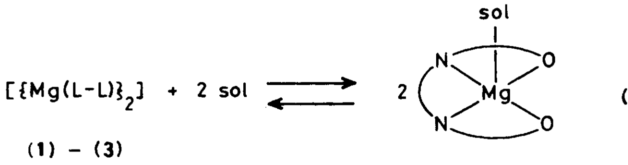
Refinement attempted in *Ama*2 stopped at $R = 0.042$ (unit weights) and did not converge on applying a weighting scheme. In addition, chemically equivalent bond distances were unacceptably different. This hypothesis was then discarded and the centrosymmetric model accepted. Final co-ordinates for the non-hydrogen atoms are given in Table 3. Metal–ligand bond distances and angles for (**1**) and (**4**) are given in Table 4. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Results and Discussion

The synthesis of magnesium chelate compounds was performed by adding a thf solution of $Mg(CH_2Ph)_2$ to a thf solution of the free ligand: equations (1)—(3).

Complexes (**2**) and (**3**) crystallized from the thf solution, while (**1**), which is significantly more soluble, was crystallized from toluene. Complexes (**1**)—(**3**) are very sensitive to hydrolysis. In spite of the very high acidity of magnesium, the C=N stretching frequency is not affected significantly, varying from 1 650 to 1 610 cm^{-1}. The absence of any thf molecule in the solid state, and the high tendency of Mg to achieve five-co-ordination [*cf.* complex (**4**)] favours dimerization for complexes (**2**) and (**3**) in the solid state. Quadridentate Schiff-base complexes are very often dimeric, though the nature of the dimer depends on the nature of the Schiff-base ligand. The complexes [{M(acen)}$_2$] (M = Fe[17] or Mn[18]) have the same structure as that of (**1**), Co–salen and Co–salphen dimers have the structure[19] proposed for complexes (**2**) and (**3**). In the latter case[19] the MN_2O_2 skeleton has a nearly planar structure. Differences in the structures of the dimers depend on the geometrical flexibility of the ligand, which is rather rigid in the case of salen and salphen.

The solid-state structure of complexes (**1**)—(**3**) may differ from that in solution of oxygen-donor solvents, because of the equilibrium depicted in equation (4) (L–L = acen, salen, or salphen; sol = thf or acetone). As a consequence, we do not know if ^1H n.m.r. spectra recorded in acetone belong either to the dimeric or the monomeric form (**A**), though we are sure that only one of the two forms is detectable in solution. Complex (**4**) occurs in the monomeric form (**A**), in which magnesium binds a thf molecule, because of the absence of oxygen-donor atoms in the macrocyclic ligand which can provide co-ordinative saturation of the metal *via* the dimerization process seen for complexes (**1**)—(**3**).



(4)

(**A**)

The structure of complex (**1**), which resembles that of iron[17] and manganese,[18] consists of centrosymmetric dimers [{Mg(acen)}$_2$] where the acen molecules are symmetrically bridging the two metal atoms (Figure 1). Selected bond distances and angles are quoted in Table 4. Magnesium is in a trigonal-bipyramidal co-ordination with the set of atoms O(2),N(1),O(1′) in the equatorial plane, and N(2) and O(1) in the axial positions. The N_2O_2 sets shows significant tetrahedral distortions ranging from −0.364(5) to 0.441(5) Å. A significant difference is observed for Mg–O(2) and Mg–O(1) distances [1.952(5) *vs.* 2.028(5) Å] as a consequence of the bridging role of the O(1) oxygen, co-ordinating the metal atoms at distances which are not significantly different [2.028(5) *vs.* 2.018(5) Å for Mg–O(1′); Mg–O and Mg–N distances fall in the usual range and the Mg···Mg′ distance is 3.047(3) Å. As a consequence of dimerization the two six-membered chelate rings have different conformations: magnesium lies nearly in the mean plane through O(2),C(11),C(10),C(9),N(2) [deviation 0.123(2) Å], while it is 0.574(2) Å out of the mean plane through O(1),C(2),C(3),C(4)N(1). The dihedral angle between these two planes is 118.0(2)°. The N(1)–C(6)–C(7)–N(2) torsion angle is −42.8(7)°, C(6) and C(7) being displaced by 0.253(7) and 0.788(7) Å respectively on the same side of the plane through Mg,N(1),N(2). A significant lengthening of the O(1)–C(2) bond

Table 4. Selected bond distances (Å) and angles (°) for complexes (**1**) and (**4**)*

	(**1**)	(**4**)		(**1**)	(**4**)
Mg–O(1)	2.028(5)	2.041(3)	Mg–N(1)	2.125(6)	2.060(2)
Mg–O(2)	1.952(5)		Mg–N(2)	2.107(5)	
Mg–O(1′)	2.018(5)				
O(2)–Mg–O(1′)	107.1(2)		Mg–O(1)–C(2)	125.7(4)	
O(2)–Mg–N(1)	131.5(2)		Mg–O(2)–C(11)	128.7(4)	
N(1)–Mg–O(1′)	121.4(2)		Mg–N(1)–C(6)	114.1(4)	
O(1)–Mg–N(2)	163.9(2)		Mg–N(1)–C(4)	125.8(4)	125.1(2)
Mg–N(2)–C(7)	108.4(4)		Mg–N(2)–C(9)	126.2(5)	
N(1)–Mg–N(1′)		79.7(1)	N(1)–Mg–N(1″)		91.6(1)
Mg–O(1)–C(7)		125.5(1)	Mg–N(1)–C(1)		108.3(1)

* Primes denote atoms at positions $1 - x, \bar{y}, \bar{z}$ [(**1**)] and $\bar{x}, y, z$ [(**2**)]; double primes atoms at $x, y, \frac{1}{2} - z$.

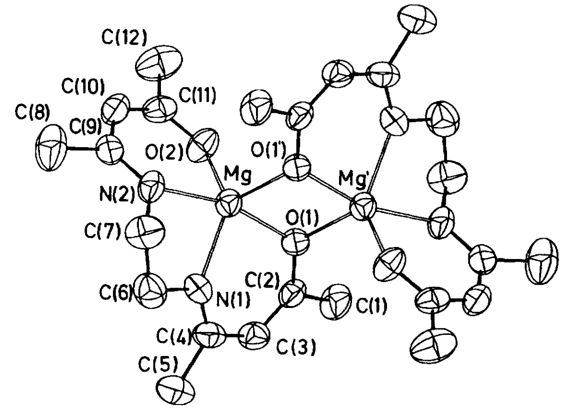


Figure 1. ORTEP View of complex (**1**) (30% probability ellipsoids)

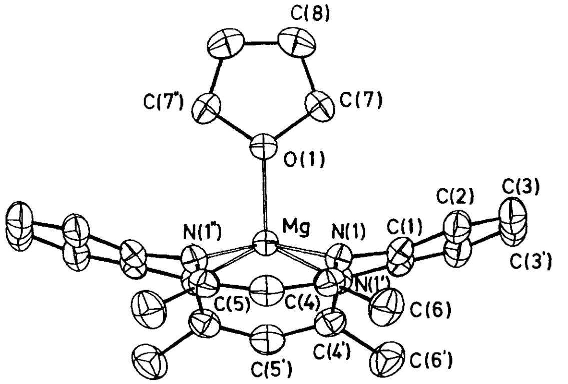


Figure 2. ORTEP View of complex (**4**) (30% probability ellipsoids)

distances is observed [1.329(7) *vs.* 1.281(8) Å for O(2)–C(11)]. All the other bond distances and angles within the acen molecule agree well with those observed in other complexes[18] and indicate a partial localization of the conjugate double bonds: C(2)–C(3) 1.346(9), N(1)–C(4) 1.308(9), C(10)–C(11) 1.374(10), N(2)–C(9) 1.289(8) Å. No intermolecular interactions other than van der Waals contacts are observed.

The reaction of dibenzylmagnesium with H_2tmdbtd afforded complex (**4**). We did not observe any reaction by the Grignard at the macrocyclic skeleton.[8] The occurrence of (**4**) with a five-co-ordinate magnesium is largely expected from the strong acidity of the metal ion which binds tightly a molecule of thf.[3,4] The 'naked' [Mg(tmdbtd)] may be used as a strong Lewis acid. The molecular structure of (**4**) was determined by *X*-ray analysis, and is shown in Figure 2; selected bond distances and angles are listed in Table 4. The molecule possesses an imposed *mm* symmetry with the tmdbtd ligand having an unusual saddle shaped conformation.[20] The five-co-ordinate magnesium atom is displaced 0.565(1) Å from the N_4 core which is perfectly planar for symmetry requirements. The oxygen atom from a thf molecule occupies the fifth co-ordination site. The magnesium–nitrogen distance [2.060(2) Å] is in good agreement with the values observed in porphyrin derivatives, as is the Mg–O(1) distance [2.041(3) Å].[3,4] The planes through the five- and six-membered chelate rings [excluding the magnesium atom which is displaced by 0.834(1) and 0.212(1) Å respectively] form dihedral angles of 10.1(1) and 31.8(1)° respectively with the N_4 plane. The intermolecular contacts correspond with normal van der Waals interactions.

Acknowledgements

We thank the U.S. Navy (Grant No. N00014-86-K-0380) and the Fonds National Suisse de la Recherche Scientifique (Grant No. 2.131—0.86) for financial support.

References

1 D. E. Fenton, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. McCleverty, Pergamon Press, Oxford, 1987, vol. 3, ch. 23.

2 J. H. Fuhrhop and K. M. Smith, in 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975, ch. 13, p. 757; J. J. Katz and J. R. Norris, *Curr. Top. Bioenerg.*, 1973, **5**, 41; K. Ballschmiter and J. J. Katz, *J. Am. Chem. Soc.*, 1969, **91**, 2661; J. J. Katz, W. Oettmeier, and N. R. Norris, *Philos. Trans. R. Soc. London B*, 1976, **273**, 227; M. S. Fischer, D. H. Templeton, A. Zalkin, and M. Calvin, *J. Am. Chem. Soc.*, 1971, **93**, 2622; R. Timkovich and A. Tulinsky, *ibid.*, 1969, **91**, 4430; H. C. Chow, R. Serlin, and C. E. Strouse, *ibid.*, 1975, **97**, 7230; C. Kratky and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1977, **33**, 545; C. Kratky, H. P. Isenring, and J. D. Dunitz, *ibid.*, p. 547.

3 G. A. Rodley and C. C. Ong, *Inorg. Chim. Acta*, 1983, **78**, 171; C. B. Storm, A. H. Corwin, R. A. Arellano, M. Martz, and R. Weintraub, *J. Am. Chem. Soc.*, 1966, **88**, 2525; K. M. Kadish and L. R. Shiue, *Inorg. Chem.*, 1982, **21**, 3623; V. McKee, C. C. Ong, and G. A. Rodley, *ibid.*, 1984, **23**, 4242; R. Bonnett, M. B. Hursthouse, K. M. Abdul Malik, and B. Mateen, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2072.

4 L. D. Spaulding, P. G. Eller, J. A. Bertrand, and R. H. Felton, *J. Am. Chem. Soc.*, 1974, **96**, 982; K. M. Barkigia, L. D. Spaulding, and J. Fajer, *Inorg. Chem.*, 1983, **22**, 349.

5 F. K. Fong and V. J. Koester, *J. Am. Chem. Soc.*, 1975, **97**, 6888; F. K. Fong, *ibid.*, p. 6890.

6 H. A. Tajmir-Riahi and M. Lotfipoor, *Spectrochim. Acta, Part A*, 1983, **39**, 167; J. M. Bellerby, J. H. Morris, and W. E. Smith, *Inorg. Chim. Acta*, 1985, **96**, 203; C. R. Saha, *J. Inorg. Nucl. Chem.*, 1980, **42**, 159.

7 S. J. Baum, B. F. Burnham, and R. A. Plane, *Proc. Natl. Acad. Sci. U.S.A.*, 1964, **52**, 1439; J. H. Fuhrhop and D. Mauzerall, *J. Am. Chem. Soc.*, 1969, **91**, 4174; A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.

8 J. Thomas, *Bull. Soc. Chim. Fr.*, 1973, 1296; *Tetrahedron Lett.*, 1975, 847.

9 V. L. Goedken and M. C. Weiss, *Inorg. Synth.*, 1980, **20**, 115; A. R. Cutler, C. S. Alleyne, and D. Dolphin, *Inorg. Chem.*, 1985, **24**, 2276.

10 S. L. Lawton and R. A. Jacobson, 'TRACER,' cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, U.S.A., 1965.

11 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.

12 G. M. Sheldrick, 'SHELX 76,' System of Crystallographic Computer Programs, University of Cambridge, 1976.

13 A. J. C. Wilson, *Nature (London)*, 1942, **150**, 151.

14 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 99; (*b*) p. 149.

16 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

17 F. Corazza, C. Floriani, and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 1987, 709 and refs. therein.

18 C. Floriani, F. Corazza, A. Chiesi-Villa, and C. Guastini, unpublished work.

19 M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1972, **9**, 311; M. Calligaris, G. Nardin, and L. Randaccio, *ibid.*, 1972, **7**, 385.

20 C. Floriani, S. Ciurli, A. Chiesi-Villa, and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 70; V. L. Goedken and J. A. Lodd, *J. Chem. Soc., Chem. Commun.*, 1982, 142; V. L. Goedken, S. M. Peng, J. A. Molin-Norris, and Y. Park, *J. Am. Chem. Soc.*, 1976, **98**, 8391.

Received 30th *December* 1987; *Paper* 7/2268