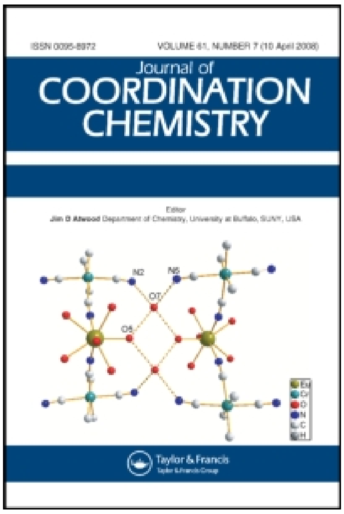

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Behaviour of Bis(Ethylacetoacetato)-Magnesium and Calcium in Solutions of Polychloromethanes. The Crystal Structure of Trinuclear Bis(Ethylacetoacetato)Magnesium

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BEHAVIOUR OF BIS(ETHYLACETOACETATO)-MAGNESIUM AND CALCIUM IN SOLUTIONS OF POLYCHLOROMETHANES. THE CRYSTAL STRUCTURE OF TRINUCLEAR BIS(ETHYLACETOACETATO)MAGNESIUM.

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IR, ^{1}H and ^{13}C NMR spectroscopic studies of 10^{-2}–10^{-3} mol dm^{-3} solutions of bis(ethylacetoacetato)-magnesium and calcium M(eacacet)$_2$, M = Mg and Ca, in CCl_4, $CHCl_3$ and $CDCl_3$ containing >0.01% H_2O or D_2O are reported. The crystal structure of Mg(eacacet)$_2$, determined by X-ray diffraction analysis, consists of a centrosymmetric trinuclear complex of the type [Mg{Mg(eacacet)$_3$}$_2$]. It is trigonal, space group $R\bar{3}$, with $a = 17.464(2)$, $c = 12.125(2)$ Å, $V = 3202$ Å^3, $Z = 3$, $D_x = 1.440$ g cm^{-3} and $R = 0.035$. Linkage of the central and terminal Mg atoms is achieved by common O atoms of the enolate groups. Spectral and structural investigations of M(eacacet)$_2$ reveal a slow isomerization to an *s-trans*-enolate and hydrolysis to ethylacetoacetate, instead of metallotropy, as reported previously.

Keywords: Ethylacetoacetate, magnesium, calcium, complex, X-ray structure, hydrolysis

INTRODUCTION

The phenomenon of metallotropy (cationotropy)[1,2] has been reported for magnesium and calcium derivatives of 3-oxo-butanoic acid ethyl ester (ethylacetoacetate, Heacacet) in chloroform. On the basis of IR data, isomerization of the *s-cis*-enolate (chelate, *Z*) into both the *s-trans*-enolate (*E*) and carbeniate (*C*) forms, according to Scheme 1, was proposed. The absence of any additional evidence to support the existence of such a phenomenon encouraged us to perform the present study using structural methods, and ^{1}H and ^{13}C NMR and IR spectroscopy.

EXPERIMENTAL

Pure Mg(eacacet)$_2$ and Ca(eacacet)$_2$ were obtained using known methods.[1,2] Crystals of Mg(eacacet)$_2$ suitable for X-ray diffraction analysis were grown by slow evaporation of a CH_2Cl_2 solution of the complex.

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Solvents and solutions

Standard solvents for spectroscopy containing different amount of water; $CHCl_3$ (0.01% and 0.05% H_2O), $CDCl_3$ (0.02% and 0.05% H_2O) and CCl_4 (0.02% H_2O) (Uvasol, Merck), were used. Tetrachloromethane (0.05% H_2O, D_2O) was obtained by three-fold treatment of CCl_4 (0.02% H_2O) with D_2O followed by distillation. Water contents were determined by Fischer's method.[3] In addition to the above, 10^{-2} mol dm^{-3} solutions of Heacacet and saturated (10^{-2}–10^{-3} mol dm^{-3}) solutions of Mg(eacacet)$_2$ and Ca(eacacet)$_2$ were prepared.[1,2]

Deuterated Heacacet was obtained by three-fold treatment of 10^{-2} mol dm^{-3} Heacacet (25 cm^3) in CCl_4 (0.05% H_2O, D_2O) with 1 cm^3 D_2O portions for 72 h.

All solvents and solutions were kept in well-stoppered vessels in the dark.

Spectroscopic measurements

Infrared spectra were recorded on Specord IR-75 (Carl Zeiss) and Perkin Elmer 983 spectrophotometers. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 FT spectrometer with external standard (TMS) at room temperature.

TABLE I

Crystal data and experimental details for structure determination of [Mg{Mg(eacacet)$_3$}$_2$].

Molecular formula	$Mg_3O_{18}C_{36}H_{54}$
Molecular weight	847.8
Crystal system	trigonal
Space group	$R\bar{3}$
a, Å	17.464(2)
c, Å	12.125(2)
V, Å^3	3202
Z	3
D_{calc}, g.cm^{-3}	1.440
μ_{calc}, cm^{-1}	1.4
F(000)	14.76
Temperature, K	292
Radiation, Å	MoKα, 0.71073
Scan technique	ω/2θ
Scan speed, °/min	2–7
Scan width	0.8 + 0.4 tanθ
sinθ/λ	0.616
$h\ k\ l$ range	$\pm h$, $\pm k$, $\pm l$
Reflections measured	4163
Reflections unique	1402
R_{int}	0.027
Reflections used ($I > 2\sigma(I)$)	879
R	0.0353
R_w	0.0442
S	1.1622
Weights	$4F_o^2/[\sigma(F_o)^2]^2$
Shift to error ratio	0.710
Maximum residual density, e Å^{-3}	0.23

Structure analysis

A colourless prism of Mg(eacacet)$_2$ with approximate dimensions $0.14 \times 0.16 \times 0.25$ mm was investigated on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKα radiation. Data were collected by the $\omega/2\theta$ scan technique. Essential crystallographic data and details of the data collection and structure determination are given in Table I. Unit cell parameters were determined by least-squares analysis of 23 reflections with $20° < \theta < 21°$. D_m was not determined. Two standard reflections were monitored every 2 h; the intensity variation was $<0.1\%$ and no decay correction was applied. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was made using a psi-scan method. The transmission factor varied from 93.7 to 99.9%.

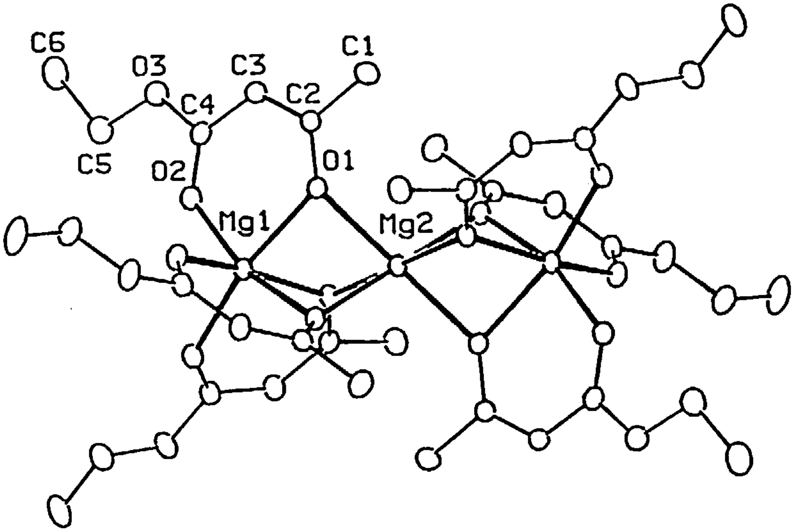


FIGURE 1 Molecular structure and numbering scheme for (Mg{Mg(eacacet)$_3$}$_2$).

TABLE II
Positional and equivalent isotropic thermal parameters with e.s.d.'s for [Mg{Mg(eacacet)$_3$}$_2$] ($B_{eq} = 4/3\ \Sigma_i\ \Sigma_j\ \beta_{ij}\ a_i\ a_j$).

Atom	x/a	y/b	z/c	B_{eq}(Å^2)
Mg1	0.0	0.0	0.2632(1)	2.81(2)
Mg2	0.0	0.0	0.5	2.70(3)
O1	0.08887(8)	0.00448(8)	0.3818(1)	3.00(3)
O2	0.02972(9)	−0.08089(9)	0.1765(1)	3.54(4)
O3	0.1044(1)	−0.1462(1)	0.1204(1)	4.46(4)
C1	0.2105(2)	0.0025(2)	0.4646(2)	4.21(6)
C2	0.1458(1)	−0.0217(1)	0.3719(2)	3.01(5)
C3	0.1500(1)	−0.0681(1)	0.2838(2)	3.62(6)
C4	0.0902(1)	−0.0966(1)	0.1931(2)	3.34(5)
C5	0.0463(2)	−0.1805(2)	0.0268(2)	4.75(7)
C6	0.0823(2)	−0.2241(2)	−0.0465(3)	6.83(9)

The structure was solved by direct methods (MULTAN 82) and refined by full-matrix least-squares based on F. All H atoms were located and refined isotropically. No correction for secondary extinction was applied. Atomic scattering factors and anomalous dispersion coefficients were used as coded in the SDP/PDP V3.0 software package. All calculations were performed on a PDP 11/44 computer. The final coordinates of the non-hydrogen atoms are listed in Table II. The atom numbering scheme is shown in Figure 1 and selected interatomic distances and bond angles are given in Table III. Listings of observed and calculated structure factors, hydrogen atom parameters and anisotropic thermal parameters are available from G.P.

TABLE III

Interatomic distances (Å) and bond angles (°) for $[Mg\{Mg(eacacet)_3\}_2]$.

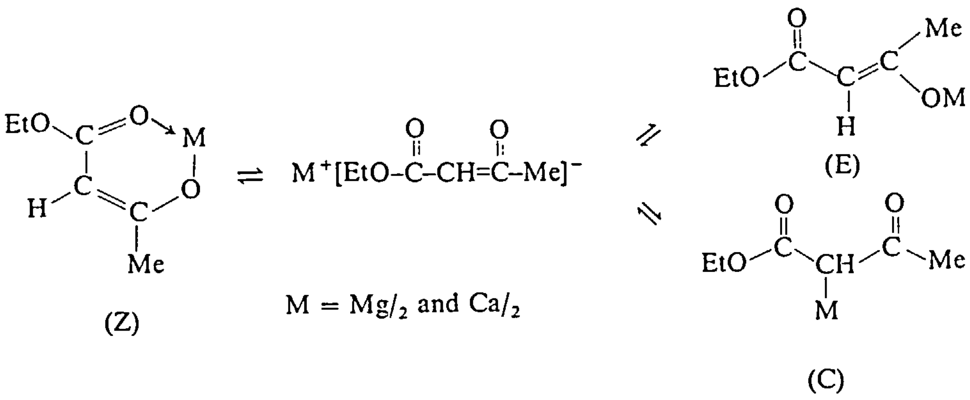
Distances			
Mg1-O1	2.088(2)	O3-C5	1.439(3)
Mg1-O2	2.026(2)	C1-C2	1.497(3)
Mg2-O1	2.085(1)	C2-C3	1.365(3)
O1-C2	1.291(3)	C3-C4	1.424(3)
O2-C4	1.234(3)	C5-C6	1.498(5)
O3-C4	1.344(3)		
Angles			
O1-Mg1-O1^{i}	77.80(7)	C4-O3-C5	117.9(3)
O1-Mg1-O2	86.90(6)	O1-C2-C1	115.9(2)
O1-Mg1-O2^{i}	99.84(5)	O1-C2-C3	124.4(2)
O1-Mg1-O2^{ii}	164.28(7)	C1-C2-C3	119.8(2)
O1-Mg2-O1^{i}	77.96(6)	C2-C3-C4	124.3(2)
O1-Mg2-O1^{iii}	102.04(6)	O2-C4-O3	119.4(2)
Mg1-O1-Mg2	86.94(6)	O2-C4-C3	127.6(2)
Mg2-O1-C2	137.8(1)	O3-C4-C3	113.1(2)
Mg1-O1-C2	127.7(1)	O3-C5-C6	106.9(3)
Mg1-O2-C4	128.1(2)		

Symmetry codes: i: $-y, x-y, z$; ii: $y-x, -x, z$; iii: $y, y-x, 1-z$.

RESULTS AND DISCUSSION

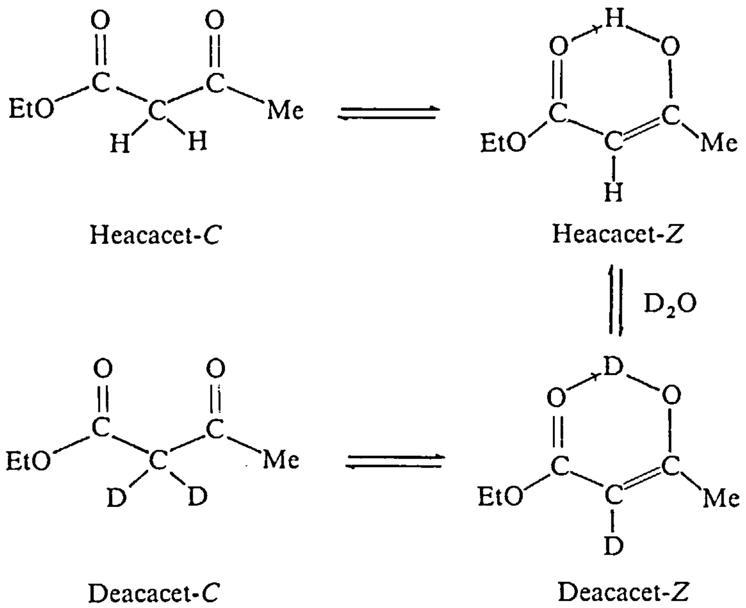
Spectroscopic investigations

As has been shown,[1,2] the IR spectra of $Mg(eacacet)_2$ and $Ca(eacacet)_2$ in the solid state differ significantly from those of $CHCl_3$ solutions kept for several hours. Previous authors have explained the observed differences *via* metallotropy as shown in Scheme 1. They have attributed the IR spectral bands to the following isomeric forms: *s-cis*-enolate (*Z*) (ν C=C–C=O at ~1640 and 1555 cm^{-1}), *s-trans*-enolate (*E*) (ν C=C at 1655 corr. 1665 cm^{-1} for Mg and Ca complexes) and carbeniate (*C*) (ν O=COEt at 1742 and ν O=CMe at 1718 cm^{-1}). Because of the identity of the observed spectral bands at 1742 and 1718 cm^{-1} with those of the free ligand Heacacet, the question arises as to whether form *C* or free ligand exists in solution.



SCHEME 1 Mechanism of metallotropy for $Mg(eacacet)_2$ and $Ca(eacacet)_2$ in $CHCl_3$ solutions according to P. Markov, C. Ivanov *et al.*[1,2]

One probable process yielding a free ligand in $CHCl_3$ solution is hydrolysis of the *Z* form. This assumption is supported by the doubling of the rate of decrease of the IR band intensities of the *Z*-form in $CHCl_3$ when the water content is increased from 0.01 to 0.05%. In order to answer the question we prepared and investigated partially deuterated Heacacet (Deacacet; Scheme 2).



SCHEME 2 Deuteriation of ethyl acetoacetate (Heacacet).

IR spectral data for Deacacet in CCl_4 (0.05% H_2O, D_2O), Heacacet in CCl_4 (0.05% H_2O) and $Mg(eacacet)_2$ both in KBr and CCl_4 (0.05% H_2O, D_2O) are given in Table IV. The $\delta(CD_2CO)$ bands at 1070, 1069 cm^{-1} in $Mg(eacacet)_2$ solution in

TABLE IV

Infrared data (cm^{-1})* for the compounds Heacacet, Deacacet and Mg(eacacet)$_2$.

Assignments	Heacacet[i]		Deacacet[i]		Mg(eacacet)$_2$[ii]	Mg(eacacet)[iii] Mg(eacacet)$_2$-*Z*
	Z	*C*	*Z*	*C*	*Z*	H- and Deacacet-*Z* and *C*
ν(C=O)ester		1744s		1742s		1744s
ν(C=O)keto		1722s		1720s		1721s
ν(C$\overset{\cdots}{-}$O)enol	1650s		1655s			1650s, (1655)sh
ν(C$\overset{\cdots}{-}$C)enol	1631s		1590m[4]			1631m, 1590w
ν(C$\overset{\cdots}{-}$C)					1631s	1631m
ν(C$\overset{\cdots}{-}$O)ester					1529s	1525w
$\delta(CH_2)$CO		1414m				1415w
ν(C$\overset{\cdots}{-}$O)					1270s, 1258s	1256m
ν(C–O)enol	1236s		1286s[5]			1236s, 1286m
$\delta(CD_2)$CO				1070m		1069w
π(O–H)	935w					934w
π(=C–H)	overlap				791m	overlap
π(O–D)			621w[6]			618w

* Intensities: s = strong, m = medium, w = weak, sh = shoulder. [i] In CCl_4. [ii] In KBr. [iii] In CCl_4 (0.05% H_2O and D_2O) 18 days after dissolution.

CCl_4 (0.05% H_2O, D_2O), can be considered as evidence for the presence of the free ligand. ^1H NMR spectra of $CDCl_3$ (0.05% H_2O) solutions of Mg(eacacet)$_2$ and Ca(eacacet)$_2$ showed signals characteristic of both *Z* and *E* isomers (see Scheme 1) and for Heacacet (Table V and Figure 2). Proton signals expected for the HC–M group in the supposed metallotropic form *C* were not found in the 14 to −7 ppm range.

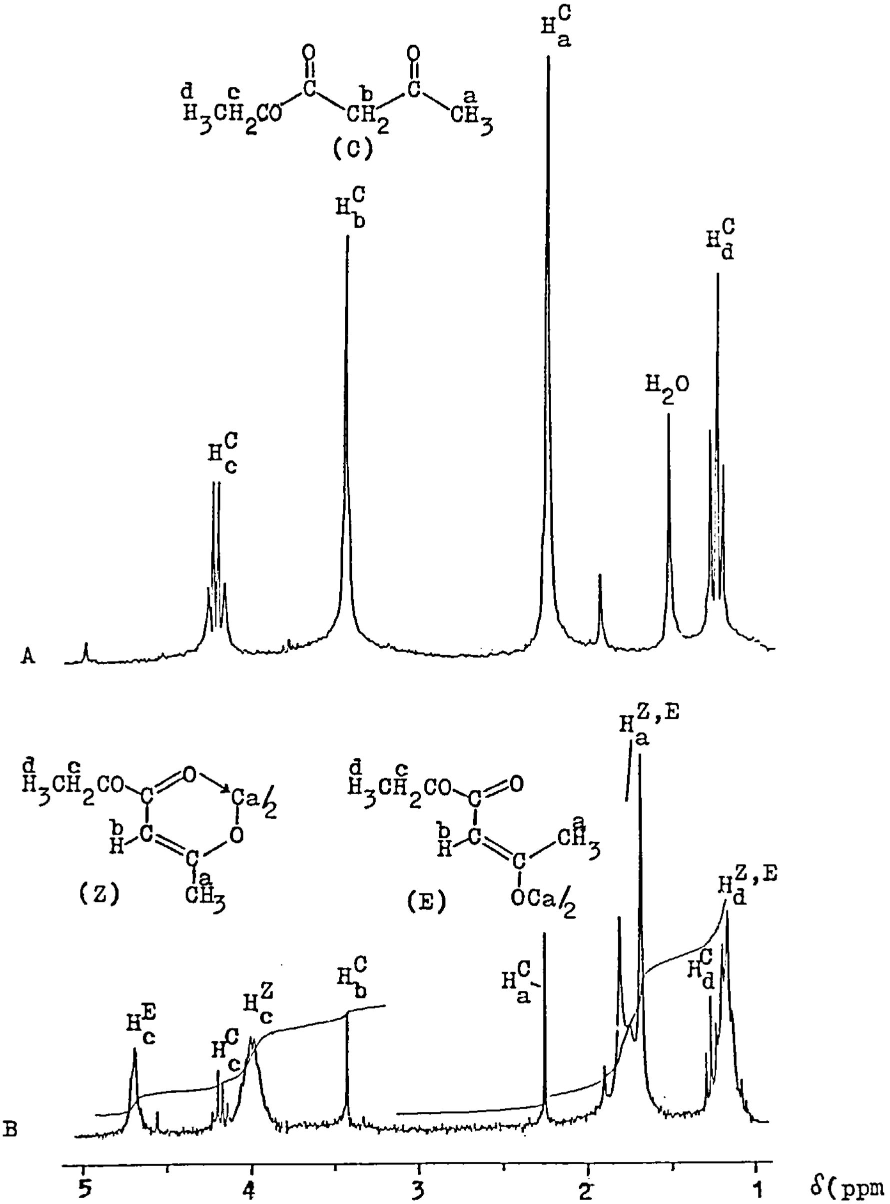


FIGURE 2 ^1H NMR spectra of A: Heacacet-*C*, 10^{-2} mol dm^{-3} in $CDCl_3$ (0.05% H_2O) and B: Ca(eacecet)$_2$, 10^{-3} mol dm^{-3} in $CDCl_3$ (0.05% H_2O), 8 h after dissolution, with signals of Ca(eacacet)$_2$–*Z*, Ca(eacacet)$_2$–*E* and Heacacet-*C*.

TABLE V

^1H NMR data for the compounds* (δ in *ppm*, J in *Hz*).

Compound	Form	δ/J	H_a**	H_b	H_c	H_d
$Mg(eacacet)_2$[i]	*Z*	δ	1.61*s*[ii]	overlap	3.47*q*	1.20*t*
		J_{HH}			7.0	7.0
	E	δ	1.94*s*	4.20*s*	3.71*q*	1.23*t*
		J_{HH}			6.5	7.0
	Heacacet-*C*	δ	2.26*s*	3.44*s*	4.19*q*	1.27*t*
		J_{HH}			7.1	7.1
$Ca(eacacet)_2$[i]	*Z*	δ	1.70*s*	overlap	4.00*m*	1.17*t*
		J_{HH}			7.0	7.0
	E	δ	1.82*s*	4.56*s*	4.70*m*	1.17*t*
		J_{HH}			7.0	7.0
	Heacacet-*C*	δ	2.26*s*	3.43*s*	4.19*q*	1.28*t*
		J_{HH}			7.1	7.1
Heacacet	*Z*[iii]	δ	1.94*s*	4.96*s*	3.72*q*	1.27*t*
		J_{HH}			7.0	7.1
	C	δ	2.26*s*	3.43*s*	4.19*q*	1.28*t*
		J_{HH}			7.2	7.1

* In $CDCl_3$ relative to Me_4Si. ** Formulae in Figure 2. [i]Two weeks after dissolution. [ii]Key: *s*—singlet, *t*—triplet, *q*—quartet, *m*—multiplet. [iii]The signal of the OH group is at 12.09 *ppm*.

The ^{13}C NMR spectrum of a saturated $CDCl_3$ (0.05% H_2O) solution of $Mg(eacacet)_2$ made after 6 months storage contained the following Heacacet signals (*C* form); $H_3C^f\text{-}C^eH_2\text{-}OC^d(O)\text{-}C^cH_2\text{-}C^b(O)\text{-}C^aH_3$: 14.1(C^f), 30.0(C^a), 50.13(C^c), 61.37(C^e), 167.0(C^d) and 199.0(C^b) ppm. In the ^{13}C NMR spectrum of Heacacet (10^{-2} mol dm^{-3} in $CDCl_3$) the respective signals are: 14.09(C^f), 30.06(C^a), 50.16(C^c), 61.37(C^e), 167.08(C^d) and 198.89(C^b) ppm. It is noteworthy that any signal characteristic of a carbon atom bonded to a Mg atom of the metallotropic form *C* is absent. Moreover, the reaction for quantitative determination of a C–Mg bond in $Mg(eacacet)_2$ with Gilman's reagent[7] was not positive. The position of the specific signals in ^1H and ^{13}C NMR spectra of $Mg(eacacet)_2$ and $Ca(eacacet)_2$ are in agreement with literature data[8,9] for other Heacacet salts.

The only argument proposed by other authors[1,2] for the reverse process (Scheme 1) has been the experimentally established recovery of the *Z* chelate forms after complete evaporation of the solvent from the $Mg(eacacet)_2$ and $Ca(eacacet)_2$ solutions (based on IR spectra of the solid residues). However, this is valid also for the hydrolytic process. We have proved experimentally that mixtures of equivalent amounts of fresh $Mg(OH)_2$ or $Ca(OH)_2$ and Heacacet give, in a short time, *Z*-$Mg(eacacet)_2$ and *Z*-$Ca(eacacet)_2$ complexes and water. Their IR spectra in nujol were identical to those obtained previously.[1,2]

Because of the expected bis-chelate stability of the $Mg(eacacet)_2$ and $Ca(eacacet)_2$ *Z* complexes, it was difficult to accept the idea of a slow hydrolytic process in $CHCl_3$, CCl_4 and $CDCl_3$. Hence, the crystal and molecular structure of the $Mg(eacacet)_2$ complex was determined.

Crystal structure of $Mg(eacacet)_2$

The crystal structure of $Mg(eacacet)_2$ consists of centrosymmetric trinuclear complexes with no intermolecular contacts between the non-hydrogen atoms of less than 3.5 Å. The terminal Mg atoms are tris-chelated in a propeller-like fashion, while the central Mg atom is surrounded by six bridging enolate oxygen atoms from six eacacet ligands (Figure 1). The whole molecule can be thought of as a species of the type $[Mg\{Mg(eacacet)_3\}_2]$. Similar metal-to-ligand arrangements have been found in trinuclear bis(acetylacetonato)-magnesium[10] and -manganese(II)[11] complexes as well as in bis(diethoxyphosphorylacetonato)-cobalt(II),[12] -nickel(II),[13] and -magnesium.[10]

The central Mg2 atom has an ideal, symmetry imposed, trigonal antiprismatic coordination with an Mg–O distance of 2.085(1) Å. The oxygen atoms around Mg1 form an octahedron, distorted towards a trigonal prism, as indicated by the twist-angle $\varphi = 47°$ between the triangular faces.[14] The bridging Mg1–O1 coordination bond (2.088(2) Å) is longer than non-bridging Mg1–O2 (2.026(2) Å; Table III). The O···O chelate bite distance is 2.819(2) Å and the separation between the bridging O atoms of the two $Mg(eacacet)_3^-$ units is 3.241(3) Å. The O···O distances in the common and outer triangular faces are 2.623(3) and 2.999(3) Å, respectively; the O1–Mg1–O2 bite angle is 86.90(6)°, the central O1–Mg2–O1 angle 77.96(6)°, and the Mg1–O1–Mg2 angle is 86.94(5)°. Local symmetry around the Mg atoms can be represented as O_h–D_{3d}–O_h for all trinculear complexes of the type $[Mg(MgL_3)_2]$, L = acetylacetonato-, ethylacetoacetato- and diethoxyphosphorylacetonato-, in contrast to the case of $[Mn\{Mn(acetylacetonato)_3\}_2]$ (D_{3h}–O_h–D_{3h}).[11] The Mg···Mg distance is 2.871 Å. Eacacet is planar to within 0.038 Å, the Mg atoms being displaced from the ligand plane by 0.24 and 1.13 Å (Mg1 and Mg2, respectively). Folding along the O···O line is to the extent of $170.6(2)^0$. A thorough examination of the bond lengths within the ligand show pronounced variation; the bridging C–O distance 1.291(3) Å is significantly longer than the non-bridging (1.234(3) Å) and the adjacent C2–C3 and C3–C4 distances are 1.365(3) and 1.424(3) Å, respectively. Such differences have been observed in hexakis(acetylacetonato)trimagnesium and -trimanganese(II) as well.

The peculiarity of the trinuclear structure of bis(ethylacetoacetato)magnesium gives us reason to suggest the following overall scheme for hydrolysis (Scheme 3).

$$\begin{tikzcd}
{[M'\{M(\text{s-cis-eacacet})_3\}]} \arrow[r, "H_2O"] \arrow[d] & {[M'\{M(\text{s-cis-eacacet})_3\}\{H_2O\}]} \arrow[dd] \\
{[M'\{M(\text{s-cis-eacacet})_2(\text{s-trans-eacacet})\}]} \arrow[dr, "H_2O"] & \\
 & {[M'\{M(\text{s-cis-eacacet})_2(\text{Heacacet})\}\{OH\}]}
\end{tikzcd}$$

$$M' = Mg\{Mg(\text{s-cis-eacacet})_3\};\ M = Mg$$

SCHEME 3 Hexakis(ethylacetoacetato)trimagnesium hydrolysis in $CHCl_3$ and CCl_4 containing >0.01% H_2O.

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