Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

INVESTIGATIONS ON ORGANOZINC COMPOUNDS
X*. COORDINATION CHEMISTRY OF ORGANOZINC COMPOUNDS RZnX: ORGANOZINC-OXYGEN DERIVATIVES OF POTENTIALLY BIDENTATE LIGANDS

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(Received February 19th, 1968)

SUMMARY

The coordination chemistry of organozinc compounds RZnOD in which OD is a bidentate ligand such as 2-methoxyethoxide (I), 2-(dimethylamino)ethoxide (II), 8-hydroxyquinolinate (III, IV), *N*-phenylsalicylaldiminate (V, VI) and acetylacetonate (VII, VIII) has been studied. With the exception of tetrameric (I) which has a cubic structure, RZnOD compounds exist as dimers (V–VIII) or trimers (II–IV) in benzene solution as a result of intermolecular Zn–O and intramolecular Zn–D bridging. Valency angle strain largely determines the degree of association, the RZnOD derivatives being dimeric if a six-membered and trimeric if a five-membered chelate ring is present. This is supported by the results of a study of $EtZnOCH_2CH_2CH_2NMe_2$ which in benzene exists as a mixture of dimeric and tetrameric species. The complex-forming behaviour of RZnOD derivatives in the presence of mono- and bidentate ligands offers valuable information on the nature of these compounds. Complexes have been characterized in which *N,N,N',N'*-tetramethylethylenediamine is thought to act as a bridging ligand.

INTRODUCTION

Whereas simple organozinc alkoxides RZnOR' are tetramers in benzene[1], lower degrees of association are observed if the group R' has high steric requirements (*e.g.* $EtZnOCHPh_2$ is trimeric[2] and $PhZnOCPh_3$ is dimeric[2] in benzene; for tert-BuZnO-tert-Bu both dimeric[3] and trimeric[4] association has been reported). For tetrameric compounds RZnOR' a cubic structure has been proposed[1] and subsequently confirmed[5] (for MeZnOMe) by X-ray crystallography.

Alkylzinc phenoxides are tetrameric also[1,4], but such compounds are dimeric and display variation in coordination behaviour if the phenoxy hydrogens are replaced by chlorine or fluorine[4].

The coordination chemistry of RZnON< derivatives (derived from oximes[2,4] and diethylhydroxylamine[4]) depends on the groups bound to nitrogen, tetrameric[2,4],

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* For Part IX see ref. 4.

hexameric[4] and more highly associated[4] structures having been observed. Organozinc derivatives of potentially bidentate alcohols, *i.e.* tetrameric methylzinc 2-methoxyethoxide[1] and trimeric methylzinc and ethylzinc 2-(dimethylamino)ethoxide[2] have recently been reported.

In the course of our study of the coordination chemistry of organozinc compounds RZnX[4,6,7] we have investigated several organozinc derivatives of monoprotic, potentially bidentate hydroxy derivatives. In the present paper our results on derivatives of 8-hydroxyquinoline, N-phenylsalicylaldimine, acetylacetone, 2-(dimethylamino)ethanol and 3-(dimethylamino)-1-propanol are reported.

RESULTS AND DISCUSSION

The various compounds prepared together with the results of molecular weight determinations as well as analytical and melting point data are listed in Table 1.

TABLE 1

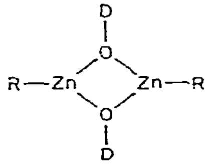
SOME ORGANOZINC DERIVATIVES OF MONOPROTIC, POTENTIALLY BIDENTATE HYDROXYL COMPOUNDS

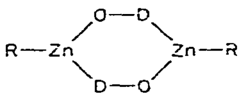
No.	Compound	M.p. (°C)	% Zn found (calcd.)	% N found (calcd.)	Molecular weight[a]			Degree of association n
					Concn. (%)	Found	Calcd.	
(I)	$PhZnOCH_2CH_2OMe$	165–166	30.51 (30.05)		1.11	874	217.6	4.01
(II)	$PhZnOCH_2CH_2NMe_2$	65	28.30 (28.34)	6.52 (6.07)	1.82	604	230.6	3.01
(III)	$EtZnOC_9H_6N$[b]	245–250	27.65 (27.48)	5.71 (5.88)	2.03	700	237.6	2.94
(IIIa)	$Zn(OC_9H_6N)_2 \cdot TMED$[b,c]	dec. 212	11.83 (11.93)	9.94 (10.21)	2.05	558	548.0	0.98
(IV)	$PhZnOC_9H_6N$[b]	dec. >183	21.08 (22.81)	4.64 (4.89)	7.63	861	286.6	3.00
(V)	$EtZnOC_6H_4$-*o*-CH=NPh	160–170	22.09 (22.49)	4.73 (4.82)	2.07	623	290.7	2.13
(Va)	$[EtZnOC_6H_4$-*o*-$CH=NPh]_2 \cdot TMED$	117	16.78 (16.85)	7.30 (7.22)	2.97	501	786.7	0.64
(VI)	$PhZnOC_6H_4$-*o*-CH=NPh	200–202	19.62 (19.30)	5.30 (5.33)	1.27	661	338.7	1.96
(VII)	EtZnOCMe=CHAc	95–98	33.86 (33.77)		3.80	303	193.5	1.60
(VIIa)	EtZnOCMe=CHAc·Py	36	23.79 (23.98)	4.14 (4.09)	6.45	289	272.6	1.06
(VIIb)	EtZnOCMe=CHAc·TMED	60–62	25.49 (25.98)	5.39 (5.57)	4.18	379	503.3	0.74
(VIII)	PhZnOCMe=CHAc	92	26.94 (27.06)		1.69	519	241.6	2.14
(IX)	$EtZnO(CH_2)_3NMe_2$	77	33.30 (33.25)	7.06 (7.13)	2.97	461[d]	196.6	2.34

[a] Molecular weights were determined by ebulliometry in benzene unless otherwise stated. For all compounds with the exception of (VII) and (VIIb) the mol. wt. observed was independent of the concentration; only one value is reported. [b] OC_9H_6N = 8-hydroxyquinolinate. [c] This compound crystallizes with one mole of crystal benzene. [d] Determined by cryometry.

As shown in Table 1 the organozinc compounds RZnOD* prepared in this study with the exception of (I) and (IX) are either dimeric or trimeric in benzene solution.

Various structural possibilities exist for compounds RZnOD. For dimeric species a structure such as (A) containing coordinatively unsaturated zinc and a vacant donor site on both oxygen and the donor atom in D does not seem probable in light of our knowledge that the zinc atom in organozinc compounds strives for tetra-coordination whenever this is possible[1,2,4,6,7]. A structure such as (B) is improbable, not only because again zinc would be tri-coordinate, but also because the greatly increased donor strength of an oxygen atom bound to an electropositive metal (*cf.* ref. 8) will strongly favour the formation of Zn–O–Zn bridges in compounds RZnOD. Zinc may become tetra-coordinate either by chelate formation [bonding from D to Zn, structure (C)] or by face to face coordination of two dimer units (A) such as occurs in simple alkylzinc alkoxides[1,5]. The formation of a tetramer, in preference to a dimer (C) has recently been observed for $MeZnOCH_2CH_2OMe$[1]. Apparently, the oxygen bound to zinc can compete successfully with the ether oxygen for the fourth coordination position of the zinc atom. However, as will be discussed below, tetra-coordination is usually obtained by chelate-type bonding resulting in structures such as (C) for dimeric and as (D) for trimeric species RZnOD. Structure (D) has recently been assigned to trimeric Me- and $EtZnCH_2CH_2NMe_2$[2].


(A)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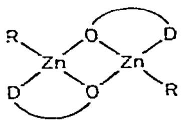
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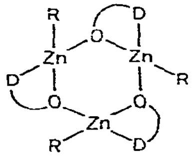
(D)

*Phenylzinc 2-methoxyethoxide (I**)*

$PhZnOCH_2CH_2OMe$ (I) like $MeZnOCH_2CH_2OMe$[1] is tetrameric in benzene solution. The zinc atom must be coordinatively saturated since neither with pyridine nor with TMED*** complex formation takes place. The observation that the chemical shift of the methoxy protons in $HOCH_2CH_2OMe$ (δ 3.22 ppm) and in $PhZnOCH_2CH_2OMe$ (δ 3.17 ppm) is very nearly the same suggests that the methoxyl group is not involved in coordination. Therefore, a cubic structure involving tetra-coordinate alkoxy-oxygen atoms similar to that proposed for the methylzinc derivative[1] is likely to apply.

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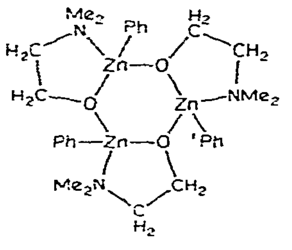
* O–D is a potentially bidentate ligand.

** Numbers correspond with those in Table 1.

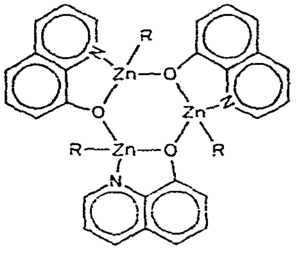
*** TMED = *N,N,N′,N′*-tetramethylethylenediamine.

Phenylzinc 2-(dimethylamino)ethoxide (II)

$PhZnOCH_2CH_2NMe_2$ (II) is trimeric in benzene solution. Since complex formation does not take place in the presence of excess of pyridine or TMED a (D)-type structure in which zinc has become tetra-coordinate by intermolecular Zn–O and intramolecular Zn–N bridging seems likely (II). Apparently, neither pyridine nor TMED is able to break the Zn–N coordinate bonds in this molecule.



(II)



(III, R = Et; IV, R = Ph)

In the PMR spectrum the $-OCH_2-$ and $-NCH_2-$ triplets (observed at δ 3.76 and 2.09 ppm) are broad at room temperature. Upon heating to 70° the triplets sharpen, indicating an opening and closing of the five-membered chelate rings or interconversion of the boat and chair form of the Zn_3O_3 ring which will not be completely flat. Similar arguments have been put forward by Coates and Ridley[2] for trimeric MeZn- and $EtZnOCH_2CH_2NMe_2$.

Ethylzinc 8-hydroxyquinolinate (III) and phenylzinc 8-hydroxyquinolinate (IV)

Both (III) and (IV) are trimeric in benzene. The donating capacity of the oxygen atoms in these compounds will be diminished by the presence of the electron-withdrawing quinolyl group (cf. similar effects in organozinc phenoxides[4]) favouring tri-coordination of oxygen. Since both compounds fail to form complexes with pyridine, a (D)-type structure in which zinc has become tetra-coordinate by intramolecular Zn–N bridging is proposed for these compounds (III, IV). The tendency of the 8-hydroxyquinolinate ligand to form chelate type complexes is, of course, well-documented[9].

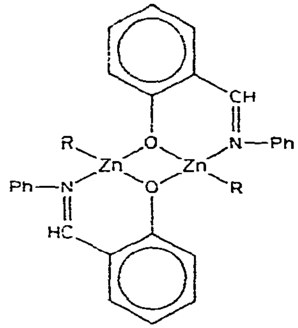
The PMR spectrum of (III) at room temperature in benzene solution shows the methylene protons as a very broad quartet at δ 0.39 ppm, whereas the triplet of the methyl protons at δ 1.38 ppm is much sharper. The broadness of the CH_2 signal may be the result of opening and closing of the relatively weakly bonded Zn_3O_3 ring (the trimer would then be kept together by the Zn–N bridges). The occurrence of boat to chair interconversion of the Zn_3O_3 ring forms an alternative explanation.

Difficulties were encountered in preparing pure (IV) because of its tendency to disproportionation in benzene solution into diphenylzinc and zinc bis(8-hydroxyquinolinate). In the presence of excess of diphenylzinc formation of the latter is effectively suppressed.

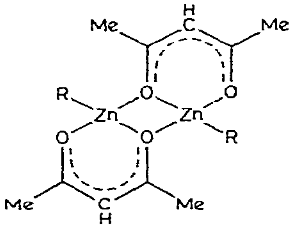
Although (III) is perfectly stable in this respect attempts to prepare its TMED complex resulted in the isolation of the 1 : 1 complex of zinc bis(8-hydroxyquinolinate) and TMED (IIIa). Whereas these phenomena are unusual for organozincoxygen derivatives similar disproportionation reactions have been reported for organozinc-nitrogen derivatives[1,10].

Ethylzinc N-phenylsalicylaldiminate (V) and phenylzinc N-phenylsalicylaldiminate (VI)

Both (V) and (VI) are dimeric in benzene solution. Again, the lack of interaction with pyridine points to a (C)-type structure with intermolecular Zn–O and intramolecular Zn–N bridges (V, VI). This structure is supported by the recently reported crystal structure analysis of dimeric zinc bis(*N*-methylsalicylaldiminate)[11]. The salicylaldiminate ligands are chelated and dimerisation is achieved via bridging through oxygen atoms of the monomers.



(V, R = Et; VI, R = Ph)

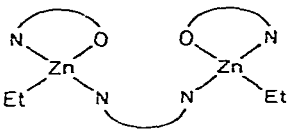


(VII, R = Et; VIII, R = Ph)

In contrast with (III) the PMR spectrum of (V) shows very sharp ethyl group absorptions, *i.e.* $\delta(CH_2)$ 0.57 ppm and $\delta(CH_3)$ 1.38 ppm. This suggests that either Zn–O coordinate bonds are stronger in this case or that the Zn_2O_2 ring has a rigid conformation.

Quite different from the behaviour of (III) the ethylzinc derivative (V) forms a crystalline complex with TMED which if recrystallized from benzene has the composition $[EtZnOC_6H_4CH{=}NPh]_2 \cdot TMED \cdot C_6H_6$ (Va). In benzene solution this complex is appreciably dissociated (Table 1).

The TMED protons of complex (Va) appear in its PMR spectrum as two singlets with intensity ratio 3:1 at 1.94 ppm (CH_3N) and 2.19 ppm (CH_2N). The observed ratio of EtZn and TMED protons was 1.63 (calculated 1.60). The PMR spectrum of TMED in benzene shows the CH_3N protons at 2.14 ppm and the CH_2N protons at 2.36 ppm. In complexes in which TMED forms a chelate ring the CH_3N singlet is generally observed at lower field than the CH_2N singlet[7] [*e.g.* for $Et_2Zn \cdot TMED$ $\delta(CH_3N) = 2.16$ ppm and $\delta(CH_2N) = 2.98$ ppm]. The observation that for (Va) the CH_3N singlet occurs at the higher field would seem to suggest that in this complex TMED does not act as a chelating ligand and a structure with a bridging TMED ligand such as schematically shown below is proposed:



Ethylzinc acetylacetonate (VII) and phenylzinc acetylacetonate (VIII)

(VIII) is dimeric in refluxing benzene. (VII) appears to be a dissociating dimer (*e.g.* $n = 1.60$ at 3.80 wt. %).

A (C)-type structure involving both inter- and intramolecular Zn–O bridging is proposed (VII, VIII).

The PMR spectrum of (VII) in benzene solution shows sharp ethyl group absorptions at δ 0.61 ppm (CH_2 quartet) and δ 1.51 ppm (CH_3 triplet). Absorptions of the acetylacetonate ligand are found at δ 1.80 ppm (CH_3 singlet) and δ 5.05 ppm (CH singlet).

The presence of chelating acetylacetonate groups in (VII) appears from the observation that the IR spectra of (VII) and of zinc bis(acetylacetonate) which has been shown to contain chelating acetylacetonate groups[12] are very similar in the carbonyl frequency region (see Table 2).

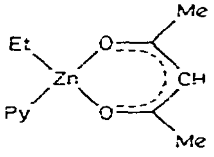
TABLE 2

IR SPECTRAL DATA OF SOME ACETYLACETONATO-ZINC DERIVATIVES[a]

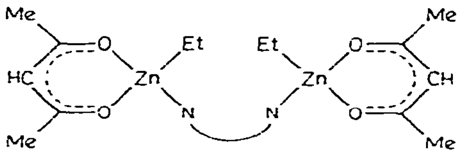
Compound	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})
$Zn(Acac)_2$	1597	1513
$[EtZnAcac]_2$ (VII)	1591	1513
$[EtZnAcac\cdot Py]_2$ (VIIa)	1595	1515
$[EtZnAcac]_2\cdot$TMED (VIIb)	1600	1515

[a] For band assignments see ref. 13.

Electron delocalization in the acetylacetonate π-system will result in reduced strength of the intermolecular Zn–O coordinate bonds. The weakness of these bonds is not only reflected in the occurrence of dissociation in the ethylzinc derivative (ethyl-substituted zinc will be a slightly worse electron acceptor than phenyl-substituted zinc), but in particular in the coordination behaviour of these compounds. In contrast with the foregoing RZnOD compounds EtZnAcac forms a monomeric 1:1 complex with pyridine (VIIa). With TMED a crystalline 2:1 complex (VIIb) is formed. The PMR spectrum shows the TMED absorptions at δ 2.08 ppm (CH_3N) and 2.16 ppm (CH_2N). As discussed for the TMED complex (Va) the high-field position of the CH_3N absorption in the PMR spectrum of (VIIb) suggests the presence of a bridging TMED ligand. The observation that ν(C=O) and ν(C=C) of the parent compound do not appreciably shift upon complexation with pyridine or TMED (see Table 2) would seem to indicate the following structures with chelating Acac ligands for these complexes:



(VII a)



(VII b)

Factors governing the degree of association of compounds RZnOD

There appears to be no general rule which may be used to predict the degree of association of compounds RZnX.

Our results show that the RZnOD derivatives in which a five-membered chelate ring is present are dimeric [(V), (VI), (VII), (VIII)], whereas those in which the chelate ring is six-membered are trimeric [(II), (III), (IV)].

The formation of dimers will be favoured relative to that of trimers or tetramers on entropy grounds. Models show that there is less steric interaction between bulky substituents in a dimer than in the corresponding trimer.

In the dimeric and trimeric RZnOD derivatives both the oxygen and the zinc atoms will be subject to some degree of valency angle strain. In the dimeric compounds the Zn–O–Zn bond angle will be ~90° (*e.g.* in $[MeZnOMe]_4$ this angle is 92°)[5]. In the trimers the Zn–O–Zn bond angle will be ~120°. This means that the remaining bond angles around the ring oxygen atoms will be greater in the dimers (~135°) than in the trimers (~120°). The steric strain introduced in the chelate ring upon dimer formation apparently can be tolerated if the ring is six-membered. However, if the chelate ring is five-membered a Zn–O–Zn bond angle of ~90° can no longer be accomodated and the considerably less strained trimer is formed.

If this reasoning is correct, chain extension of trimeric $EtZnOCH_2CH_2NMe_2$ with one carbon atom should result in dimeric rather than trimeric association, since a six-membered chelate ring can be formed.

The molecular weight of newly synthesized ethylzinc 3-(dimethylamino)-propoxide $EtZnOCH_2CH_2CH_2NMe_2$ (IX), determined by cryometry in benzene, was found to be 461 at 1.29 wt. %, *i.e.* the degree of association is 2.33. No concentration dependence could be detected. The PMR spectrum in benzene showed double sets of absorptions for all kinds of protons present (see Table 3). The intensity ratio of the two sets of signals was found to be 7:3. If it is assumed that in solution a mixture of dimeric and tetrameric species is present, the ratio of dimers and tetramers as calculated from the observed molecular weight is 7:3. This assumption would account for the observed PMR spectrum, the more intense set of signals being due to the dimer. If a mixture of dimeric and trimeric species is assumed to be present, no such correlation is found. The presence of a dissociating trimer is excluded by the lack of concentration dependence of the molecular weight.

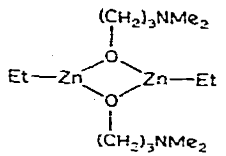
TABLE 3

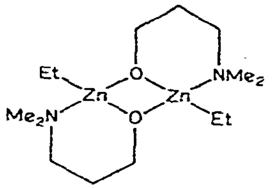
SOME PMR-SPECTRAL DATA FOR 3-(DIMETHYLAMINO)-1-PROPANOL AND ETHYLZINC 3-(DIMETHYLAMINO)-PROPOXIDE (IX)[a]

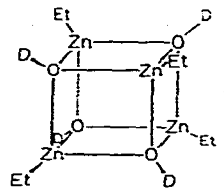
Compound	$\delta(CH_2Zn)$	$\delta(CH_3)$	$\delta(OCH_2)$	$\delta(NCH_3)$
$HO(CH_2)_3NMe_2$			3.53	2.01
Dimeric (IX)[(IXb)]	0.45	1.75	3.93	2.12
Tetrameric (IX)[(IXc)]	0.50	1.70	3.97	2.04

[a] δ in ppm downfield from tetramethylsilane (benzene, 27°).

Upon reacting $EtZnOCH_2CH_2CH_2NMe_2$ with methyl iodide in benzene solution a white precipitate with the composition $EtZnO(CH_2)_3NMe_2 \cdot MeI$ formed slowly. When this reaction was followed by PMR spectroscopy the set of absorption attributable to the tetramer could be seen to disappear slowly, whereas the signals connected with the dimer remained unaffected. Apparently, in the presence of methyl iodide the tetramer is precipitated from the solution as its quaternary ammonium salt. Since dimethylamino-nitrogen coordinated to zinc is not reactive towards methyl iodide[2], this result can be rationalized in terms of the dimethylamino group being coordinated in the dimer and free in the tetramer.


(IX a)


(IX b)


(IX c: D = $(CH_2)_3NMe_2$)

Coordination saturation in the dimer unit (IXa) may occur either by chelate-type Zn–N coordinate bonding (structure (IXb) or by face to face coordination of two units (IXa) via Zn–O bridges (structure IXc). Our results are in agreement with the dimeric species having structure (IXb) and the tetrameric species having structure (IXc).

Since the PMR spectrum of (IXb) remains unaffected upon addition of methyl iodide an equilibrium between (IXb) and (IXc) either does not exist or is established very slowly. It has not been possible to change the ratio of the two species by varying the method of synthesis. An explanation of this unusual behaviour cannot be given.

The observation that both species occurring in solution of $EtZnOCH_2CH_2CH_2NMe_2$ contain Zn_2O_2 rings whereas Zn_3O_3 rings are conspicuously absent supports our hypothesis that the occurrence of valency angle strain largely determines the degree of association of compounds RZnOD.

EXPERIMENTAL

Experimental techniques are identical to those described in ref. 4.

Synthesis of organozinc compounds RZnOD (Table 1)

The RZnOD derivatives were synthesized by the following standard procedure. A 10% solution of the hydroxyl derivative in benzene is added slowly with stirring to a 10% solution of either Et_2Zn or Ph_2Zn in benzene, which is cooled down to ~10°. Whereas Ph_2Zn was reacted in a 1 : 1 molar ratio, a 10% excess of Et_2Zn was normally used. In all cases a spontaneous, slightly exothermic reaction occurred. The temperature of the reaction mixture was not allowed to rise above 25° during the addition of the hydroxyl derivative. After completion of the addition, the mixture was heated for 15 min at 50°. Thereafter, volatile components were removed *in vacuo* and the crystalline residue recrystallized from n-hexane.

(V) and (III) which are only slightly soluble in benzene have been recrystallized from this solvent. The synthesis of (IV) is always attended by the formation of some benzene-insoluble zinc bis(8-hydroxyquinolinate), which is removed by filtration after cooling to 10°. The isolation of (IV) was performed as described in the general procedure.

Synthesis of pyridine and TMED complexes (Table 1)

A ~10% excess of pyridine or TMED was added in one portion to a ~10% solution of the compound RZnOD in benzene. If complex formation occurred, a slight evolution of heat could be observed.

(VII) + Py and (VII) + TMED. The resulting clear solution was stirred for

some minutes and thereafter the solvent and excess of complexing agent were evaporated *in vacuo*. The complexes (VIIa) and (VIIb) were recrystallized from n-hexane.

(V)+TMED. The complex (Va) crystallized from the benzene solution and was recrystallized from benzene.

(III)+TMED. TMED was added to a warm (70°) solution of (III) in benzene. Upon cooling $Zn(OC_9H_6N)_2 \cdot TMED$ (IIIa) crystallized from the solution. It was recrystallized from benzene.

ACKNOWLEDGEMENTS

Financial support by the International Lead Zinc Research Organization, Inc. (Dr. S. F. Radtke) and by Billiton–M&T Chemische Industrie N.V. is gratefully acknowledged. The authors wish to thank Professor G. J. M. van der Kerk for his stimulating interest.

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