182. Crystal Structure of Metal-Ion Complexes with neutral noncyclic Ionophores

by **Katarina Neupert-Laves** and **Max Dobler**

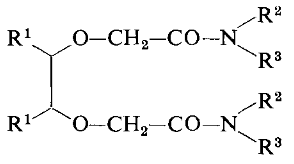
Laboratorium für organische Chemie der
Eidgenössischen Technischen Hochschule Zürich, CH-8092 Zürich

(25.V.77)

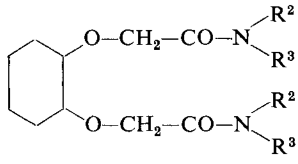
Summary

Crystal structure determinations of two metal-ion complexes with noncyclic ionophores are reported: (i) $CaCl_2$ complex of N,N,N′,N′-Tetrapropyl-3,6-dioxaoctane diamide, space group Fddd, $a = 14.659$, $b = 19.616$, $c = 33.173$ Å; (ii) $MnBr_2$ complex of N,N,N′,N′-Tetrapropyl-1,2-cyclohexylenedioxydiacetamide, space group $I\bar{4}$, $a = b = 11.695$, $c = 21.299$ Å.

Introduction. - A number of electrically neutral, lipophilic, complexing agents behave as carriers (ionophores) for the transport of ions through bulk membranes [1] and have been utilized as ion-selective components in liquid membrane electrodes [2]. In the search for compounds with higher ion-selectivity, especially for Ca^{2+}, the behaviour of several noncyclic ligands in ion-selective membrane electrodes was investigated [3]. The compounds are of the type



(A)



(B)

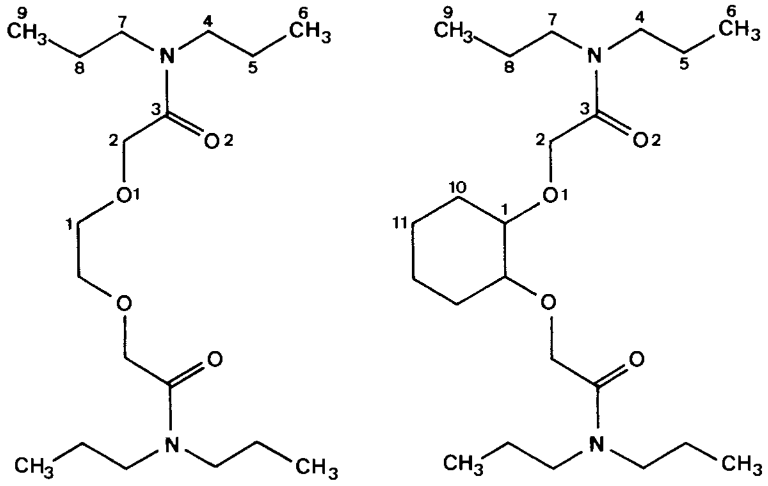
with $R^1 = H$ or CH_3, R^2, R^3 = alkyl (sometimes aryl) or ester groups, and the ring may be either saturated or aromatic. The ligands (**A**) are known [4] to induce selectivity for Ca^{2+} in membranes and to transport this ion through bulk membranes. In order to investigate the influence of structural changes in the neighbourhood of the ether oxygen atoms, various substituents (*e.g.* (**B**)) were introduced at the $-CH_2-CH_2$-bridge. Since the nature of metal complexes with such ligands was only partially known, we have carried out X-ray analyses of two, $Ca(LI)_2Cl_2$ and $Mn(LII)_2MnBr_4$ (see *Scheme*), which could be obtained in crystalline form[1]).

Coordination. - In both crystals, the metal ions occur in special positions and are coordinated to the four ether oxygen atoms and the four carbonyl oxygen atoms of a pair of symmetry-equivalent ligands. The Ca^{2+} complex crystallizes in the

---

[1]) We thank Prof. *W. Simon* for the Ca^{2+} and Prof. *I. J. Borowitz* for the Mn^{2+} complex.

Scheme



L I L II

orthorhombic space group Fddd, with the Ca^{2+} ion at (1/8, 1/8, 1/8), a site of local 2 2 2 (D_2) symmetry. The Mn^{2+} complex crystallizes in the tetragonal space group $I\bar{4}$, with the Mn^{2+} ion at (0, 1/2, 1/4), a site of local $\bar{4}$ (S_4) symmetry. Thus in both complexes, the asymmetric unit consists of only half of a ligand molecule. In spite of the different site-symmetries of the metal ions, their coordination polyhedra are very similar *(Fig. 1)*. In both cases, we have a trigonal dodecahedron in which the four ether oxygen atoms (O(1)) form the apices of an elongated tetrahedron, the four carbonyl oxygen atoms (O(2)) a flattened tetrahedron; the M ... O(1) distances are longer than the M ... O(2) distances.

A tetrahedron with 2 2 2 symmetry (Ca^{2+} complex) is described by four parameters - three O ... M ... O angles (of which only two are independent) and a M ... O distance. For the O(1) tetrahedron the O ... M ... O angles are $\theta_1 = 65.4°$, $\theta_2 = 131.9°$ and $\theta_3 = 138.5°$ (related by the equation $\cos\theta_1 + \cos\theta_2 + \cos\theta_3 = -1$) and the M ... O distance is 2.462 Å, the corresponding sum of ionic radii being 2.39 Å (O, 1.40 Å; Ca^{2+}, 0.99 Å). For the O(2) tetrahedron the angles are $\theta_1 = 81.0°$, $\theta_2 = 100.9°$ and $\theta_3 = 165.6°$, and the distance is 2.364 Å.

In the Mn^{2+} complex, where the site-symmetry is $\bar{4}$, the individual tetrahedra have D_{2d} symmetry; for each, only two angles (one independent) and one distance are required. The O(1) ... M ... O(1) angles are $\theta_1 = 67.3°$, $\theta_2 = 133.9°$ (related by $\cos\theta_1 + 2\cos\theta_2 = -1$) with a M ... O(1) distance of 2.370 Å (sum of ionic radii 2.20 Å, Mn^{2+}, 0.80 Å); for the O(2) tetrahedron $\theta_1 = 92.3°$, $\theta_2 = 156.8°$ with a M ... O(2) distance of 2.185 Å.

The highest possible symmetry for a trigonal dodecahedron is $\bar{4}2m$ (D_{2d}), with 18 edges in 4 different classes, 2(a), 4(b), 4(c), 8(d) and two types of corners, **A** and **B**. In the Ca^{2+} complex (D_2) there are two different groups of (b) and (d) edges, in the Mn^{2+} complex (S_4) two different groups of (d) edges *(Table 1)*.

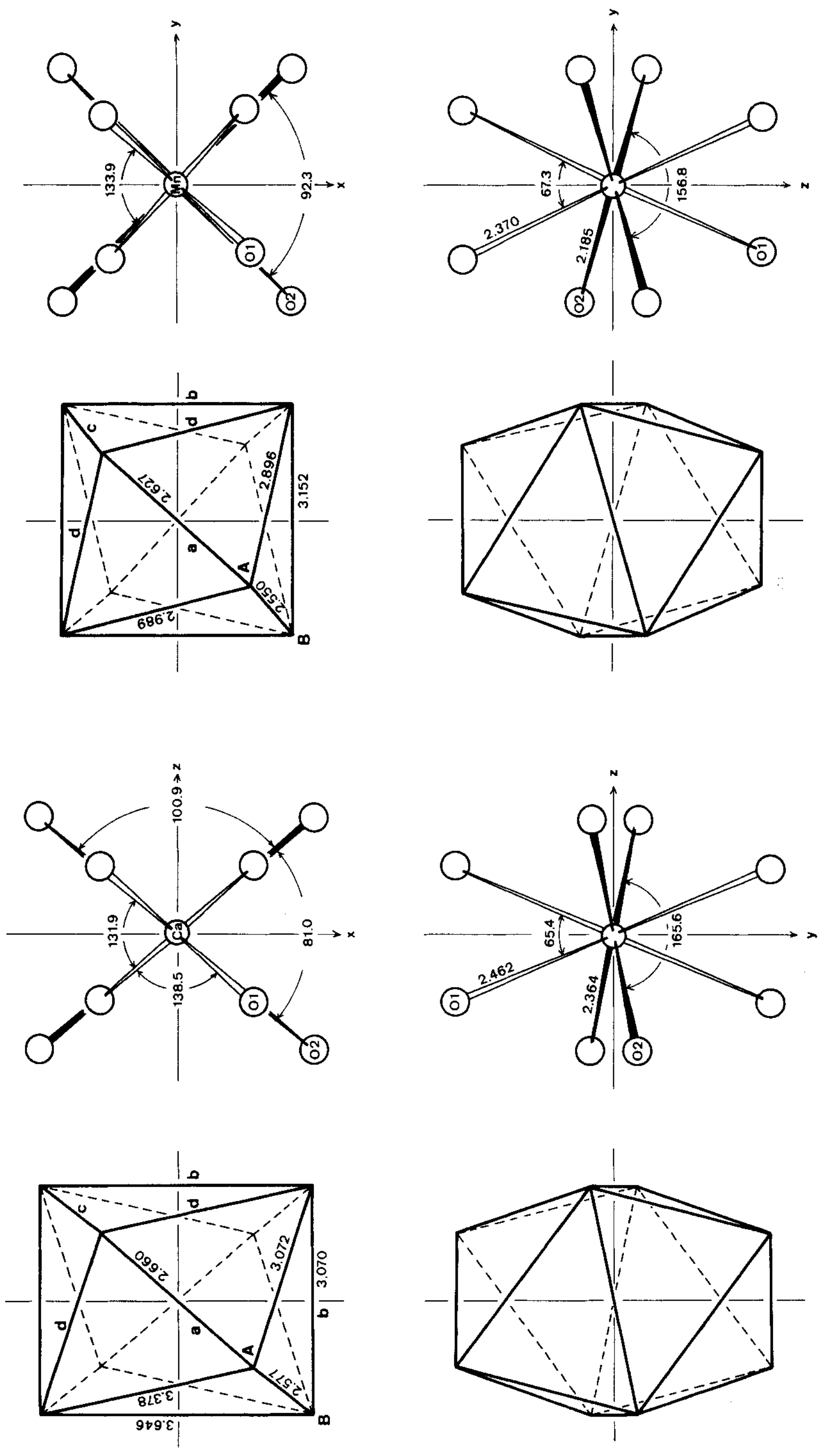


Fig. 1. *Coordination geometries for the Ca^{2+} complex* (left) *and the Mn^{2+} complex* (right). For the Mn^{2+} complex, the axes shown are rotated by 3.8° around the z axis in a clockwise direction from the crystallographic axes

Table 1. *Geometry of coordination dodecahedra for the Ca^{2+} and the Mn^{2+} complexes*

	Ca^{2+}	Mn^{2+}		Ca^{2+}	Mn^{2+}
(a)	2.660	2.627	(d)	3.072, 3.378	2.896, 2.989
(b)	3.646, 3.070	3.152	M...**A**	2.462	2.370
(c)	2.577	2.550	M...**B**	2.364	2.185

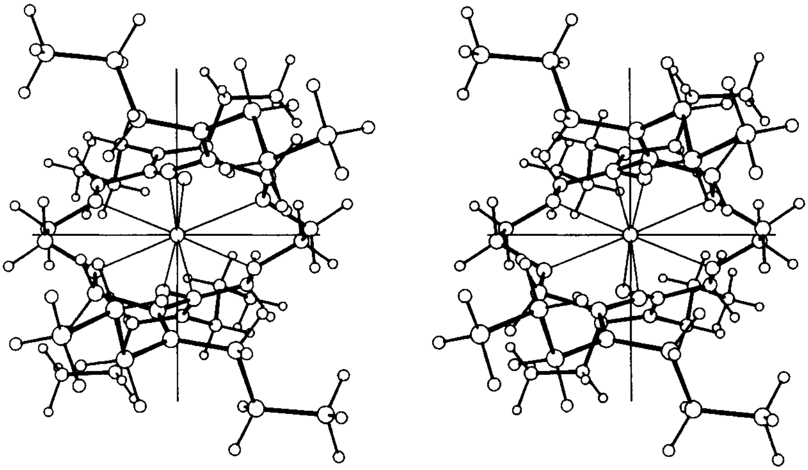


Fig. 2. *Stereoscopic view of the Ca^{2+} complex looking down the crystallographic* a *axis*

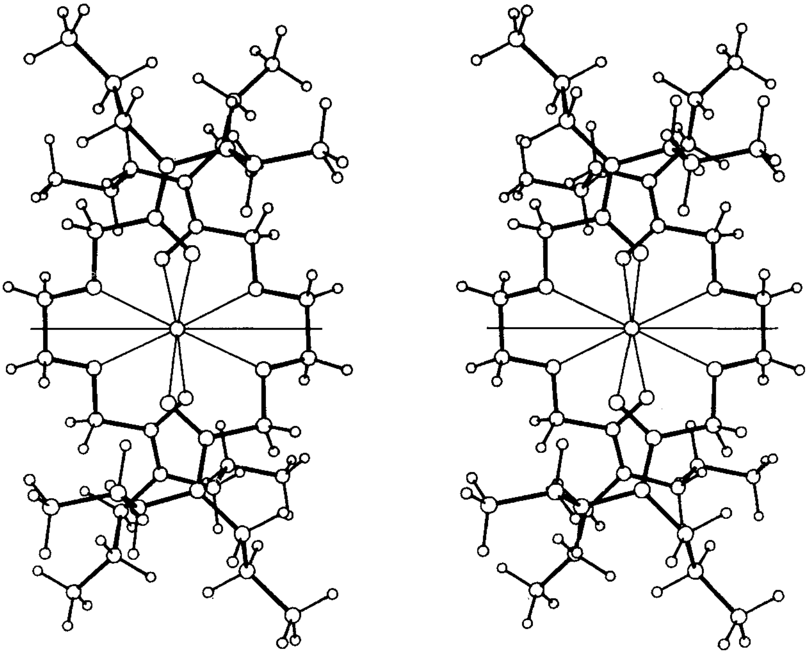


Fig. 3. *Stereoscopic view of the Ca^{2+} complex looking down the crystallographic* c *axis*

The ether oxygen atoms O(1) occupy sites **A**, the carbonyl oxygens O(2) sites **B**. *Silverton & Hoard* [5] have pointed out that, in general, smaller ligating atoms go to **A** sites, larger ones to **B** sites. However, when **A** and **B** sites are occupied by atoms of the same size, as in the $\mathrm{Zr(C_2O_4)_2^{4-}}$complex [6], M ... **B** distances are shorter than M ... **A** ones. This is also found here. It is remarkable that the two tetrahedra of ether and carbonyl oxygen atoms are in almost the same orientation: In the Ca^{2+} complex they are rotated by 1.1° against each other, in the Mn^{2+} complex by 2.8° (the Mn^{2+} coordination therefore has approximate $\bar{4}2m$ symmetry!).

The Crystal Structures. - The crystal structure of $\mathrm{Ca(LI)_2Cl_2}$ is depicted in *Fig. 2* and *3*. The complex has crystallographic 2 2 2 symmetry and thus the

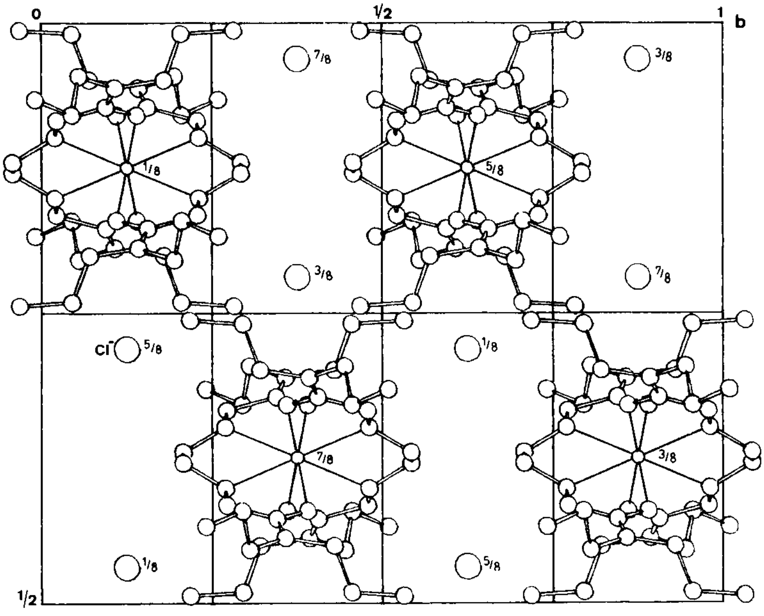


Fig. 4. *Packing of the Ca^{2+} complex in the unit cell*

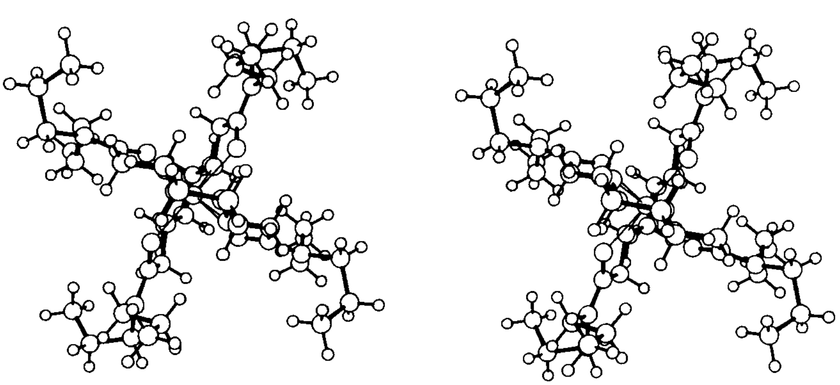


Fig. 5. *Stereoscopic view of the Mn^{2+} complex looking down the $\bar{4}$ (crystallographic* c*) axis*

asymmetric unit is one half of a ligand molecule. *Fig. 4* shows the packing. The space between the complex cations is filled with the Cl^- ions in the special positions (1/8, 1/8, 0.469). In the refinement of this structure some residual electron density ($2\ e\text{Å}^{-3}$) was found at positions (3/8, – 1/8, z) with z ~ 1/8. The explanation of this electron density peak at 3.1 Å from the Cl^- ion is not clear; it might be due to an included water molecule. In the structure analysis, this peak was treated as an oxygen atom of half-weight.

The $Mn(LII)_2MnBr_4$ structure (space group $I\bar{4}$) is shown in *Fig. 5* and *6*. The packing is depicted in *Fig. 7*. There are two types of Mn^{2+} ions present in the cell: the ones complexed by two ligand molecules sit on the $\bar{4}$ axis at special positions

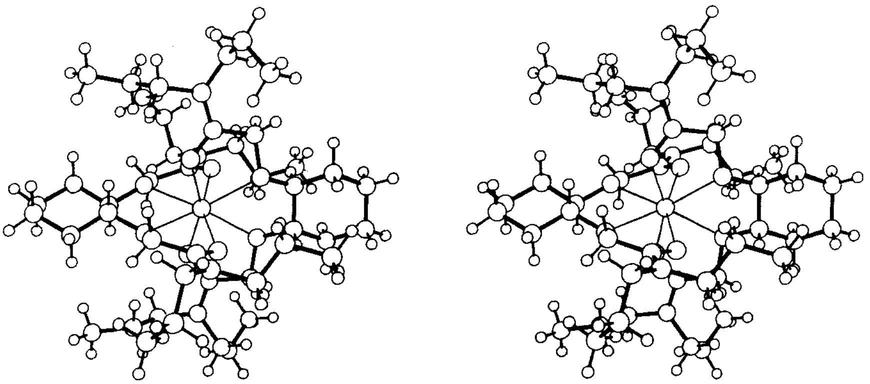


Fig. 6. *Stereoscopic view of the Mn^{2+} complex looking down the crystallographic* a *axis*

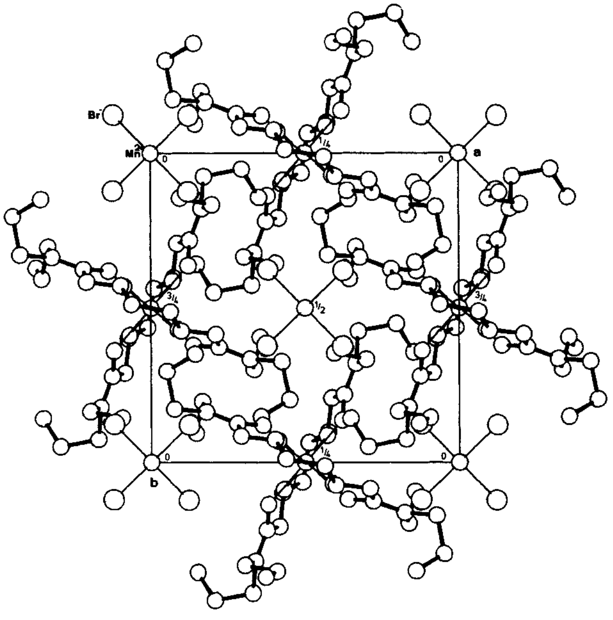


Fig. 7. *Packing of the Mn^{2+} complex in the unit cell*

(0, 1/2, 1/4), the others, surrounded by four Br^- ions in a tetrahedral arrangement, at special positions (0, 0, 0). The Br...Mn...Br angles are 110.1° and 108.2°, the Mn^{2+}...Br^- distance 2.50 Å, considerably shorter than the sum of the ionic radii (Mn^{2+}, 0.80 Å; Br^-, 1.95 Å). The Br^-...Br^- edge distances of 4.10 Å and 4.06 Å show that the Br^- ions at the apices of the tetrahedron are in contact (sum of ionic radii 3.90 Å). In neither structure are there any abnormally short intermolecular contacts.

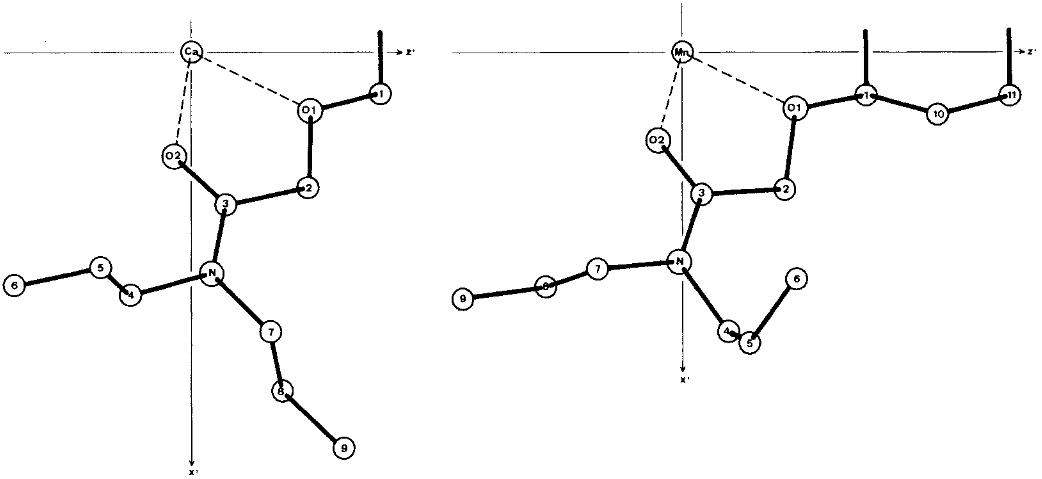


Fig. 8. *Comparison of the structures of the* Ca^{2+} (left) *and* Mn^{2+} *complex* (right). In the Mn^{2+} complex $x' = x\cos\theta + y\sin\theta$, $y' = -x\sin\theta + y\cos\theta$, with $\theta = 3.8°$

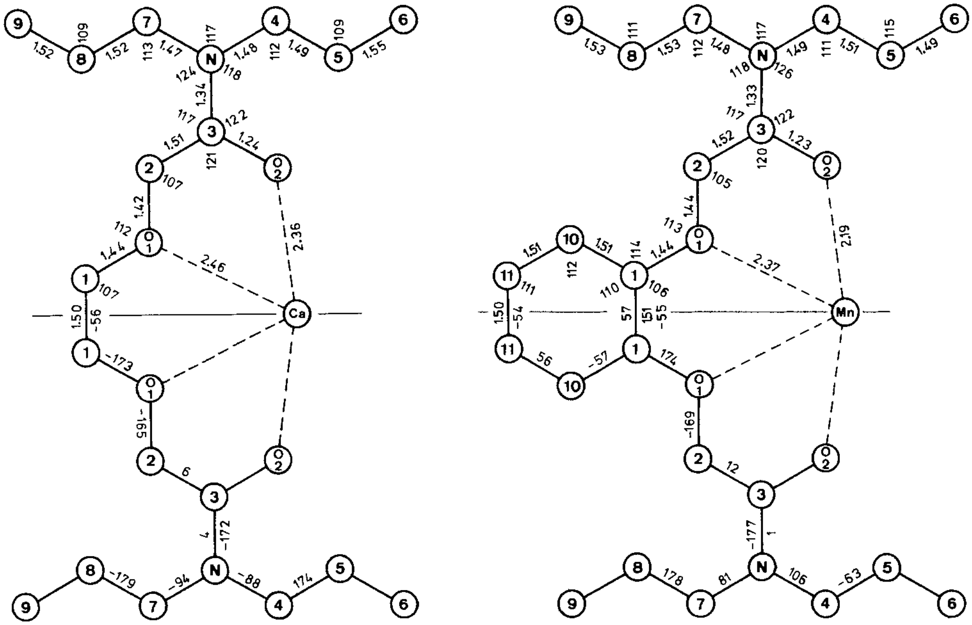


Fig. 9. *Molecular geometries for the* Ca^{2+} *complex* (left) *and the* Mn^{2+} *complex* (right). On the upper half bond lengths and angles are indicated, on the lower half torsion angles.

Fig. 8 shows projections of the two complex ions, *Fig. 9* their molecular geometries. It is evident that the parts of the ligands which hold the complexing oxygen atoms are in essentially the same conformation, while the flexible propyl side-chains have different conformations.

Inspection of the torsion angles shows that the atoms C(1′), C(1), O(1), C(2), C(3) and O(2) are approximately in a plane (the torsion angles do not deviate more than 12° from 0° or 180°). Space-filling models show that there is much room for the accomodation of the side-chains at the nitrogen atoms, so that it seems possible to introduce other side-chains without disturbing the ligand geometry too much.

Selectivity. - Extensive experimental investigations of ion-selectivity in liquid membrane electrodes [3] and of complex formation in ethanol [7] have been reported. Although the results are far from giving a clear picture for the molecular basis of selectivity of such noncyclic neutral ligands, some general trends may be deduced: (i) increase in the dielectric constant of the membrane phase leads to a preference of divalent *versus* monovalent cations of a given size; (ii) increase in polarity of the groups at the $-CH_2-CH_2$-bridge of the ligands has the same effect and also enhances the selectivity of small *versus* large cations of the same charge. On this basis, the following 'design criteria' for ligands were proposed, with special reference to the small Ca^{2+} (0.99 Å) and the larger Ba^{2+} (1.35 Å): for a high preference of Ca^{2+} over Ba^{2+}, small polar substituent constant for R^1 (high dipole moment of ligand group) and/or synclinal arrangement of the ether oxygen atoms; for a high preference of Ba^{2+} over Ca^{2+}, high polar substituent constant for R^1 (small dipole moment of ligand group) and/or syn-periplanar arrangement [3]. Both crystal structures examined here have torsion angles of about 60° around the C(1′)–C(1) bond and show a marked preference for Ca^{2+} in membrane phases of high dielectric constant. If this torsion angle is changed to 0° (synplanar arrangement) the O(1′) ... O(1) distance is reduced from 2.66 Å to 2.34 Å (*van der Waals* radius of oxygen 1.40 Å!). To offer a better complexing geometry for the larger Ba^{2+} cation, despite the shorter O ... O distance, one therefore has to assume a radical change in overall conformation. To complicate matters further, it was shown that there is no simple correlation between the selectivity behaviour in liquid membranes and the stability constants of the complexes in ethanol [7]. The possible existence of other than 1:2 complexes in liquid membranes cannot, of course, be excluded. Crystal structure determinations of Ca^{2+} and Ba^{2+} complexes with the same ligands may provide further elucidation.

Experimental. - a) $Ca(LI)_2Cl_2$: Calcium chloride complex of N,N,N′,N′-tetrapropyl-2,2′-dioxaoctanediamide, $C_{36}H_{72}N_4O_8CaCl_2$ (Mol.-Wt. 800). Orthorhombic, $a = 14.659(5)$, $b = 19.616(5)$, $c = 33.173(7)$ Å, U = 9539 Å^3, Z = 8. Space group Fddd (D_{2h}^{24}), $D_x = 1.11$.

b) $Mn(LII)_2MnBr_4$: Manganese bromide complex of *trans*-N,N,N′,N′-tetrapropyl-1,1′-cyclohexylenedioxydiacetamide, $C_{44}H_{84}Br_4Mn_2N_4O_8$ (Mol.-Wt. 1226.7). Tetragonal, $a = b = 11.695(4)$, $c = 21.299(5)$ Å, U = 2913 Å^3, Z = 2. Space group $I\bar{4}$ (S_4^2), $D_m = 1.40$, $D_x = 1.40$.

Cell constants were obtained from diffractometer measurements (Mo*Ka* radiation).

Data Collection. - Intensities for both structures were measured with a computer-controlled diffractometer (Nonius CAD4, graphite-monochromatized Mo*Ka* radiation). In the range $\theta \langle 25°$ all reflections were measured, in the range $25° \langle \theta \langle 28°$ only those judged by a preliminary scan to have significant intensity.

a) $Ca(LI)_2Cl_2$: The 3200 intensity measurements obtained were processed in the usual way, yielding 1642 unique reflections with $F_o > 3\sigma(F_o)$. Absorption corrections were not applied ($\mu_{Mo} = 2.9\ cm^{-1}$).

b) $Mn(LII)_2MnBr_4$: The 2070 intensity measurements yielded 1066 unique reflections with $F_o > 3\sigma(F_o)$. Absorption corrections were not applied ($\mu_{Mo} = 34.1\ cm^{-1}$).

Table 2. *Fractional coordinates* (estimated standard deviation × 10^4 in parentheses) *and calculated hydrogen atom fractional coordinates for* $Ca(LI)_2Cl_2$

	x	y	z		x	y	z
Ca^{2+}	0.1250(-)	0.1250(-)	0.1250(-)	H(11)	0.215	−0.043	0.149
Cl^-	0.1250(-)	0.1250(-)	0.4689(1)	H(12)	0.195	−0.087	0.102
O(1)	0.1935(2)	0.0194(1)	0.0987(1)	H(21)	0.332	0.005	0.108
O(2)	0.2477(2)	0.1401(1)	0.0796(1)	H(22)	0.292	−0.012	0.058
C(1)	0.1752(3)	−0.0426(2)	0.1203(2)	H(41)	0.380	0.212	0.073
C(2)	0.2848(3)	0.0216(2)	0.0842(1)	H(42)	0.486	0.186	0.050
C(3)	0.3045(3)	0.0945(2)	0.0727(1)	H(51)	0.305	0.196	0.006
C(4)	0.4113(3)	0.1795(2)	0.0493(2)	H(52)	0.415	0.178	−0.015
C(5)	0.3791(5)	0.2050(3)	0.0095(2)	H(61)	0.375	0.301	−0.023
C(6)	0.3996(5)	0.2822(3)	0.0064(2)	H(62)	0.472	0.290	0.009
C(7)	0.4539(3)	0.0551(2)	0.0459(1)	H(63)	0.362	0.308	0.030
C(8)	0.5235(3)	0.0443(3)	0.0793(2)	H(71)	0.418	0.006	0.040
C(9)	0.5918(3)	−0.0093(3)	0.0660(2)	H(72)	0.490	0.071	0.018
N	0.3856(3)	0.1075(2)	0.0560(1)	H(81)	0.490	0.026	0.107
O res.[a])	0.3750(-)	−0.1250(-)	0.1260(4)	H(82)	0.560	0.092	0.085
				H(91)	0.643	−0.017	0.090
				H(92)	0.626	0.009	0.038
				H(93)	0.555	−0.057	0.060

[a]) Occupation factor = 0.5, $U_{iso} = 0.135$.

Table 3. *Anisotropic vibrational parameters for* $Ca(LI)_2Cl_2$, *expressed in the form*
$\exp(-2\pi(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl))$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca^{2+}	0.041	0.035	0.050	0	0	0
Cl^-	0.066	0.048	0.095	−0.004	0	0
O(1)	0.048	0.041	0.071	−0.001	0.015	−0.001
O(2)	0.060	0.047	0.073	0.004	0.019	0.005
C(1)	0.068	0.038	0.110	0.004	0.034	0.008
C(2)	0.049	0.047	0.071	−0.001	0.017	−0.002
C(3)	0.053	0.053	0.053	−0.006	0.007	−0.002
C(4)	0.061	0.067	0.081	−0.010	0.013	0.007
C(5)	0.094	0.082	0.083	0.004	0.009	0.012
C(6)	0.133	0.085	0.124	0.008	0.028	0.036
C(7)	0.045	0.064	0.064	−0.001	0.012	−0.004
C(8)	0.060	0.090	0.069	−0.001	−0.005	−0.007
C(9)	0.059	0.104	0.089	0.009	−0.007	0
N	0.052	0.052	0.072	−0.007	0.013	0.002

Table 4. *Fractional coordinates* (estimated standard deviation × 10^4 in parentheses) *and calculated hydrogen atom fractional coordinates for* $Mn(LII)_2MnBr_4$

	x	y	z		x	y	z
Mn^{2+}_1	0 (-)	0.5 (-)	0.25 (-)	H(1)	0.107	0.565	0.399
Mn^{2+}_2	0 (-)	0 (-)	0 (-)	H(21)	0.252	0.489	0.340
Br^-	0.1240(1)	0.1212(1)	0.0689(1)	H(22)	0.240	0.354	0.363
O(1)	0.0880(5)	0.4302(5)	0.3426(3)	H(41)	0.493	0.359	0.263
O(2)	0.1377(5)	0.3794(6)	0.2294(3)	H(42)	0.412	0.374	0.327
C(1)	0.0637(8)	0.4895(8)	0.4003(4)	H(51)	0.458	0.158	0.264
C(2)	0.2091(8)	0.4146(8)	0.3324(4)	H(52)	0.522	0.201	0.330
C(3)	0.2199(7)	0.3739(7)	0.2651(4)	H(61)	0.348	0.193	0.383
C(4)	0.4249(9)	0.3272(11)	0.2869(5)	H(62)	0.283	0.150	0.317
C(5)	0.4488(12)	0.2038(12)	0.3041(7)	H(63)	0.373	0.064	0.355
C(6)	0.3572(15)	0.1481(12)	0.3423(7)	H(71)	0.404	0.249	0.176
C(7)	0.3343(9)	0.3019(9)	0.1802(5)	H(72)	0.263	0.260	0.166
C(8)	0.3548(11)	0.4053(12)	0.1380(5)	H(81)	0.283	0.457	0.140
C(9)	0.3732(16)	0.3695(17)	0.0699(7)	H(82)	0.423	0.450	0.154
C(10)	0.0982(9)	0.4258(10)	0.4587(4)	H(91)	0.444	0.319	0.067
C(11)	0.0629(10)	0.4882(13)	0.5178(4)	H(92)	0.303	0.326	0.054
N	0.3213(6)	0.3354(7)	0.2468(4)	H(93)	0.385	0.440	0.041
				H(101)	0.185	0.414	0.458
				H(102)	0.059	0.347	0.458
				H(111)	0.106	0.566	0.519
				H(112)	0.085	0.442	0.556

Table 5. *Anisotropic vibrational parameters for* $Mn(LII)_2MnBr_4$, *expressed in the form* $\exp(-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl))$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn^{2+}_1	0.037	0.037	0.027	0	0	0
Mn^{2+}_2	0.049	0.049	0.036	0	0	0
Br^-	0.065	0.090	0.078	0.009	−0.018	−0.035
O(1)	0.047	0.049	0.028	−0.002	−0.003	−0.005
O(2)	0.046	0.053	0.037	0.008	−0.008	−0.003
C(1)	0.048	0.052	0.035	0	0.006	−0.004
C(2)	0.045	0.060	0.041	0.009	−0.011	−0.011
C(3)	0.043	0.041	0.036	0.001	0.004	0.001
C(4)	0.044	0.085	0.072	0.011	−0.010	−0.016
C(5)	0.078	0.086	0.093	0.036	−0.036	−0.010
C(6)	0.134	0.082	0.076	0.010	−0.041	0.008
C(7)	0.048	0.071	0.048	0.009	−0.004	−0.009
C(8)	0.084	0.108	0.064	−0.027	0.012	0.004
C(9)	0.133	0.177	0.088	−0.021	0.043	0.024
C(10)	0.051	0.085	0.038	0	−0.008	−0.001
C(11)	0.071	0.123	0.036	0.012	−0.003	0.010
N	0.047	0.060	0.045	−0.001	−0.008	−0.009

Structure Analysis. - a) $Ca(LI)_2Cl_2$: Direct methods (program MULTAN 74 [8]) yielded an E-map in which positions of atoms O(I), O(2), C(2), C(3), N, Ca^{2+} and Cl^- could be deduced. A difference synthesis then revealed all side-chain atoms. Refinement was carried out by full-matrix least-squares analysis (four cycles with isotropic, six cycles with anisotropic temperature factors for all non hydrogen atoms) and checked by two difference syntheses. In the latter, all hydrogen atoms could be located, but calculated positions (assumptions: CH_2, local C_{2v} symmetry, HCH angle 109°, H–C distance 1.1 Å, CH_3 groups staggered) were used in the structure factor calculations. Residual electron density of $\sim 2 e Å^{-3}$ at (3/8, $-1/8$, z) with $z \sim 1/8$ was interpreted as an oxygen atom with occupancy factor 0.5, possibly from included H_2O; for this atom, only the z coordinate and isotropic temperature factor were refined. The final R factor, based on the 1642 reflections with $F_o > 3\sigma(F_o)$, was 0.057.

b) $Mn(LII)_2MnBr_4$: The positions of two independent Mn^{2+} ions in the cell and of the Br^- ion were deduced from a *Patterson* synthesis. A *Fourier* map based on the phases from these ions revealed the positions of atoms O(1), O(2), C(1), C(2), C(3), C(10) and N; a further *Fourier* map completed the structure determination. Refinement was achieved by full-matrix least-squares analysis (two cycles with isotropic, six cycles with anisotropic temperature factors) checked by three difference syntheses. All hydrogen atoms could be located in the final difference synthesis but calculated positions were used and not refined. The final R factor based on the 1066 reflections with $F_o > 3\sigma(F_o)$ was 0.041.

Results. - Fractional coordinates, calculated hydrogen atom positions and vibrational parameters for both structures are given in *Tables 2-5*. Standard deviations were estimated by inversion of the least-squares normal equations. Bond lengths and angles and torsion angles are given in *Fig. 9*. Standard deviations for C–C, C–O and C–N bonds are 0.005-0.009 Å in the Ca^{2+} complex and 0.010-0.021 Å for the Mn^{2+} complex²). Corresponding standard deviations in angles are 0.3-0.5° and 0.6-1.2° respectively.

REFERENCES

[1] *P. Wuhrmann, A. P. Thoma & W. Simon,* Chimia *27,* 637 (1973).
[2] *W. Simon, W. E. Morf & P. Ch. Meier,* Structure and Bonding, *16,* 113 (1973).
[3] *D. Ammann, R. Bissig, M. Güggi, E. Pretsch, W. Simon, I. J. Borowitz & L. Weiss,* Helv. *58,* 1535 (1975).
[4] *D. Ammann, E. Pretsch & W. Simon,* Helv. *56,* 1780 (1973).
[5] *J. L. Hoard & J. V. Silverton,* Inorg. Chemistry *2,* 235 (1963).
[6] *G. L. Glen, J. V. Silverton & J. L. Hoard,* Inorg. Chemistry *2,* 250 (1963).
[7] *N. N. L. Kirsch,* Diss. ETH No. 5842 (1976); *N. N. L. Kirsch & W. Simon,* Helv. *59,* 357 (1976).
[8] *P. Main, M. M. Woolfson & G. Germain,* MULTAN 74, University of York, England 1974.

---

²) A table of observed structure amplitudes is available on request.