

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-10 COMPLEXES OF MACROCYCLIC POLYETHER

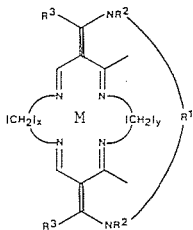
DIAMIDES. By J. Hašek, J. Ondráček, and K. Huml. Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Praha, Czechoslovakia.

(I) Complex of 7,19-dibenzyl-2,2,3,3-tetramethyl-7,19-diaza-1,4,10,13,16-pentaoxacycloheptacosane-6,20-dione with strontium tetra(4-chlorophenyl)borate and nitromethane(2:1:2:2), monoclinic, $P2_1/c$, $a=33.88(1)$, $b=11.639(2)$, $c=16.839(3)\text{Å}$, $\beta=120.23(2)^\circ$, $Z=2$, $2(C_{32}H_{46}N_2O_7)$. $\cdot Sr \cdot 2(C_6H_5Cl)_4 \cdot 2CH_3NO_2$. Crystals obtained by very slow evaporation have to be kept in a capillary. The refinement of non-H atoms with anisotropic temperature factors gave $R=0.10$ for 7752 reflections and 676 refined parameters. Two ligand molecules are coordinated by both carbonyl and two etheric oxygens to the cation lying in the centre of symmetry. Distances $Sr \dots O$ are 2.503(6), 2.486(6), 2.756(5), 2.615(6)Å. Three etheric oxygens have no contact to Sr.

(II) The complex (I), where Sr was replaced by Ca, gave poorly defined crystals showing diffuse reflections. Intensity statistics proposed space group $P1$, $a=14.68(2)$, $b=17.28(2)$, $c=23.97(5)\text{Å}$, $\alpha=80.1(1)^\circ$, $\beta=83.0(1)^\circ$, $\gamma=68.8(1)^\circ$, $Z=2$. The favourable effect of methyl substituents of the macrocycle in 2,3 positions on the selectivity for calcium in PVC membranes, studied by Petránek and Ryba (*Anal. Chim. Acta*, 1981, 128, 129), can be explained by changes of rigidity of the ethylene oxide bridge between carbonyl groups and by hindrances in forming direct contacts of the cation to the oxygens from the opposite side of macroring.

09.4-11 SYSTEMATICS OF METAL CYCLIDENE LACUNAR STRUCTURES. By N. W. Alcock, Department of Chemistry, University of Warwick, Coventry, CV4 7AL, England, and D. H. Busch, Department of Chemistry, Ohio State University, Columbus, Ohio 43210, U.S.A.

The transition metal complexes of the cyclidene unit (I) have as their key structural feature a void between the metal and the R^1 chain. Both the size of this void and its chemical nature can be adjusted by changing R^1 , and chemical studies have shown that with appropriate metal ions (especially Fe(II), Co(II), Ni(II)), these complexes can (a) bind O_2 reversibly and (b) incorporate organic substrate molecules with the potentiality of carrying out chemical reactions within the cavity. Some 20 crystal structures of this group of compounds have now been determined, and these structural results will be analysed. They also include a precursor, in which R^1 is absent, which throws light on the ease of formation of the complexes, and dimers in which R^1 is a complete metal cyclidene macrocycle.



$R_1 = (CH_2)_n$, $n = 4-8$, $m-$, p -xylyl, etc.

$R_2 = H$, CH_3 , alkyl, $-CH_2C_6H_5$,

$R_3 = H$, CH_3 , alkyl, C_6H_5 , etc.

$x, y = 2$ or 3

$M = Ni, Fe, Co, Mn$.

09.4-12 THE CRYSTAL STRUCTURE OF S-CIS-DIAQUA [BIS(2-PYRIDYL)-3,6-DITHIAOCTANE] COBALT(II) DIPERCHLORATE.

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The crystals of the $[Co(C_{16}H_{20}N_2S_2)(H_2O)_2](ClO_4)_2$ compound are monoclinic, space group $P2_1/n$, $Z = 4$ with $a = 11.676(4)$, $b = 13.357(4)$, $c = 15.835(6)\text{Å}$, $\beta = 107.33(3)^\circ$, $V = 2357.4\text{Å}^3$, $D_x = 1.686\text{Mg m}^{-3}$. 7681 reflections collected on a diffractometer using graphite monochromated $MoK\alpha$. 3179 reflections observed $I \geq 3\sigma(I)$. The structure was refined to a final R value of 0.053.

The compound is built up to discrete $[Co(C_{16}H_{20}N_2S_2)(H_2O)_2]^{2+}$ and ClO_4^- ions. In the distorted octahedral cations a single ligand molecule is coordinated to one Co via N and S atoms, forming one five-membered chelate ring ($CoSC_2S$) and two six-membered rings ($CoSC_3N$).

The two remaining coordination positions are occupied by water molecules. The perchlorate ions exhibit the expected tetrahedral geometry though somewhat deformed. They are H-bonded to H_2O coordinated molecules.

