

58. SJEZD CHEMICKÝCH SPOLEČNOSTÍ – DODATKY

METAL COMPLEXES WITH MIXED S-DONOR LIGANDS – A ROUTE VIA SILANETHIOLATES

ANNA KROPIDŁOWSKA and **BARBARA BECKER**

*Department of Inorganic Chemistry, Chemical Faculty, Gdańsk University of Technology, G. Narutowicza Str. 11/12, 80-952 Gdańsk, Poland
annakrop@chem.pg.gda.pl*

Sulfur containing compounds *e.g.* thiolates, dithiocarbamates or thioureas are often used as ligands in coordination chemistry¹. They have gained wide interest because of their versatile applications varying from molecular biology to material engineering. The use of metal silanethiolates is, however, much less recognized. Numerous complexes containing sulfur ligands were described, nevertheless these with mixed S-donor ligands are still scarce. This prompted us to undertake a systematic studies on preparation of metal complexes with sulfur-rich centers. Tri-*tert*-butoxysilanethiolates of Cd²⁺, Zn³⁺, Cu⁴⁺, Pb⁵⁺, Hg⁶⁺, Ag⁷⁺ and Co⁸⁺ were chosen as a source of metal atom and salts of dithiocarbamic acid, *e.g.*, Et₂NC(S)SNa, C₄H₈NC(S)SNH₄ served as sources of additional S-donor ligands.

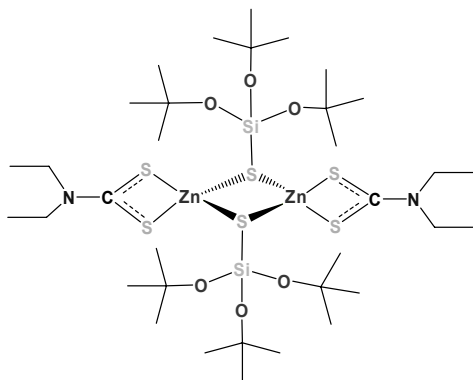


Fig. 1. Suggested structure of mixed S-donor ligand complex

Different methods and reaction conditions were tried. In the case of Ag complex only unchanged substrate was recovered. Silanethiolate complexes of Hg, Co, Pb and Cu gave respective dithiocarbamates, as it was confirmed using X-ray diffraction measurements. Direct reaction between metal silanethiolate complex and dithiocarbamate salt proved to be the most promising route in the case of Zn(II) and Cd(II) compounds. Elemental analysis and spectral data suggest that in these cases complexes with mixed S-donor ligands have been obtained (Fig. 1).

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INFLUENCE OF MANGANESE(II) SILANETHIOLATE WITH 1,10-PHENANTHROLINE ON PROPERTIES OF NATURAL RUBBER VULCANIZATES

ANNA KROPIDŁOWSKA^a, **ALEKSANDRA MAKOCKA**^b, and **MICHAŁ STRANKOWSKI**^b

^a*Department of Inorganic Chemistry, ^bDepartment of Polymer Technology, Chemical Faculty, Gdańsk University of Technology, Narutowicza Str. 11/12, 80-952 Gdańsk, Poland
annakrop@chem.pg.gda.pl*

From the ancient Greeks to modern day scientists, chemists have investigated natural materials and devised ways to synthesize new compositions and their blends. Since 1830 vulcanization was used to greatly improve the durability and utility of natural rubber. It is closely associated with development of new, efficient additives. In this group S-donor metal complexes, *e.g.* dithiocarbamates and xanthates play very important role, since they can improve vulcanization rate. It was the reason why we decide to examine the effect of heteroleptic silanethiolate complexes of manganese(II) with chelating N-donor ligands on properties of natural rubber vulcanizates.

Rubber blends were obtained using natural caoutchouc, chalk, sulfur, thiuram accelerator, ZnO activator and machine oil as softener. All components were mixed using rolling mill. We found that addition of bis(tri-*tert*-butoxysilanethiolato)(1,10-phenanthroline)manganese(II) complex noticeably influenced vulcanization time. When 0.5–2 g of metal complex (per each 100 g of caoutchouc) was introduced into rubber mixture vulcanization time decreased about 2–3 orders of magnitude without deterioration of sample properties, as it was revealed using mechanical measurements. In fact mechanical properties were even improved (higher elongation and stress at break, see Fig. 1). Also resilience and hardness

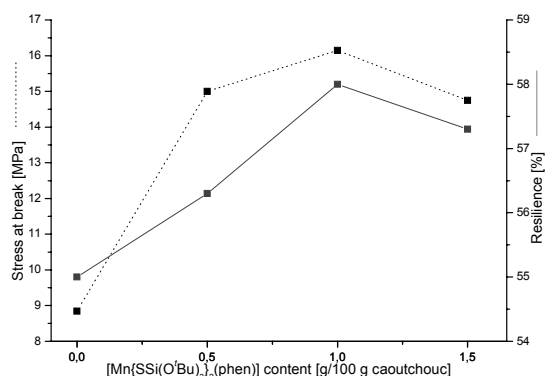


Fig. 1. Samples vulcanized 10 minutes – mechanical properties

of material were increased. However, addition of more than 3 phr of $[\text{Mn}\{\text{SSi}(\text{O}'\text{Bu})_3\}_2(\text{phen})]$ made the vulcanizate soften.

Our studies revealed that silanethiolate complexes of manganese(II) do not act as direct accelerators, nevertheless they can be used as vulcanization activating agents.

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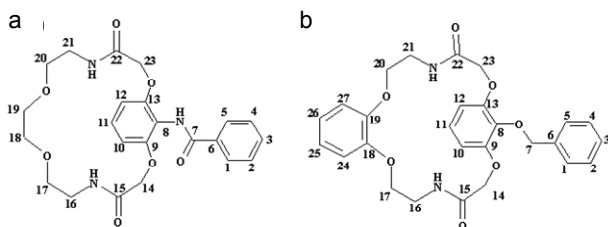
SEARCH OF NATURE OF PLANAR CHIRALITY FOR PENDANT BENZODIAZACORONANDS IN THE SOLID STATE.

JUSTYNA PACHOLCZYK^a, JAROSŁAW KALISIAK^b,
JANUSZ JURCZAK^b, and MAREK
J. POTRZEBOWSKI^a

^a Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland,

^b Polish Academy of Sciences, Institute of Organic Chemistry, Kasprzaka 44/52, 01-244, Warsaw, Poland

Chiral crystals formed from achiral molecules have recently received a great deal of attention due to their attractive structural properties and prospective applications in chemistry. For instance, such compounds can be used as



Scheme 1. Structure of compounds 1 (a) and 2 (b) with numbering system

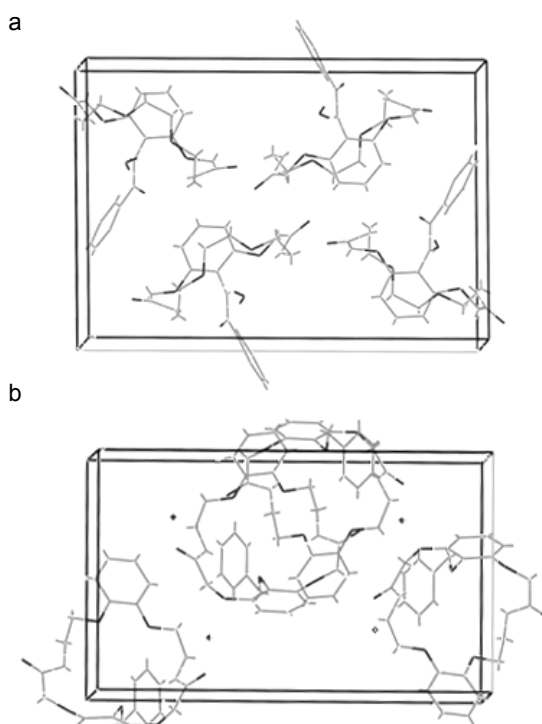


Fig. 3. Crystal lattice packing of compound 1 (a) and 2 (b)

ligands in enantioselective reactions or models to investigate molecular recognition. Understanding of details which govern the process of formation of chiral crystals, chiral induction and mechanism of spontaneous resolution of racemic compounds is one of the most general questions touching the problem of origin of life. Several research groups have intensively investigated this area trying to rationalize experimental observations and establish the rules, which allow to predict tendency to form of chiral crystals. The important contribution comes from Koshima laboratory, who recently summarized the state of art on the field of chiral crystallization of achiral organic compounds. It has been concluded that there are three important requirements for the formation of chiral crystals from achiral species; first, the generation of chirality by the rotation of bonds, second the generation of chirality by helical arrangement and third the formation of a head-to-head stacking columnar arrangement. If one or more conditions is fulfilled the formation of chiral crystals is expected.

As a part of our continuing interests in problem of formation of chiral crystals with planar chirality in this presentation we will present structural studies for two diazacoronnands shown in Scheme 1. Molecule 1 with *N*-benzoyl pendant group crystallizes in nonchiral $P2_1/n$ space group while compound 2 with *O*-benzoyl pendant

group crystallizes in chiral $P2_12_12_1$ space group. It is apparent from Scheme 1 that for both compounds macrocycles are also different. The major aim of our project is understanding of origin of distinction between these compounds and answer the question what is a crucial factor which force sample 2 to form chiral crystals. For such purpose NMR spectroscopy is found to be technique of choice. Some properties of crystals in the solid state and new applications of NMR spectroscopy will be presented. The correlation between X-ray crystallography, solid state NMR and theoretical calculations of NMR parameters will be referred.

OPTIMIZATION OF MALDI-TOF MS CONDITIONS FOR THE ANALYSIS OF STAR-SHAPED POLYLACTIDES

ANNA SROKA, M. SOCHACKI, S. OLEJNICZAK, M. J. POTRZEBOWSKI, and T. BIELA

*Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland
asroka@cbmm.lodz.pl*

Aliphatic star-shaped polylactides are biocompatible and biodegradable as their linear counterparts. These polymers are supposed to be a quite interesting because of the high number of end groups that increase with increasing of the number of arms and they can be employed in the drug delivery systems. Additionally, the hydrodynamic volume and viscosity of star-shaped polymers are lower than the hydrodynamic volume and viscosity of linear polymers with the same molar mass, thus, the melting point of these polymers are also lower.

Matrix Assisted Laser Desorption/Ionization - Time of Flight Mass Spectroscopy (MALDI TOF MS) is very useful technique for star-shaped polymers analysis, however it is required to find appropriate conditions for the efficient desorption/ionization process. For the condition optimization, two model compounds were chosen: “one arm” PLA (linear polymer with the star-shaped core) with $M_n=3100$, and “five arms” PLA with $M_n=10\ 000$. The influence of the crystal structure of four matrixes (1,8,9-trihydroxyanthracen (DT), 2,5-dihydroxybenzoic acid (DHB), 2-(4-hydroxyphenylazo)-benzoic acid (HABA), trans-3-indoleacrylic acid (IAA) and added the salt (sodium iodide, sodium chloride, lithium chloride, and potassium chloride) mixed with different amount of the star-shaped polymers was investigated. The co-crystallization of the matrix with the analyzed polymer in the presence of varying inorganic salts was monitored by means of the solid-state ^{13}C CP/MAS NMR spectroscopy and DSC (Differential Scanning Calorimetry).

The results describing of the influence of kind of using matrix and salt on the quality of MALDI spectra allowed us to verify our predictions and to suggest some rules for determination of the best matrix/salts conditions for star-shaped polylactides analysis.

FLAME RETARDANTS

MALGORZATA M. ZAITZ^{a,b}, CARL-ERIC WILÉN^b, and MELANIE AUBERT^b

^a Jagiellonian University, Department of Chemical Technology, R. Ingardena 3, 30-060 Kraków, Poland, ^b Åbo Akademi, Department of Polymer Chemistry Biskopsgatan 8, 205 00 Åbo, Finland

Modern society is built with a wide range of combustible materials. Dangerous, big fires can easily start from one spark or just a small flame. Many types of both natural and synthetic materials used in transportation, and other industrial and domestic applications should therefore be incombustible or made with such materials that are more difficult to ignite and burn. Agents that reduce combustibility and rate of flame propagation in polymer materials are known as fire (or flame) retardants. Classical flame retardants are based on halogenated, phosphorous, nitrogen, silicon-containing additives. The function of flame retardants can be distinguished as two main mechanism types: first for non-organic additives and second one for organic. Both of them are frequently used together in order to achieve synergism.

The most common use in industry have flame retardants consisting bromine-antimony and phosphorous-bromine combinations. Recent research has showed that aforementioned flame retardants have been identified as environmental contaminants that can be found in alarmingly high and increasing concentrations in tissue and blood of humans as well as in wildlife from Europe, Japan, North America and even Arctic regions.

This means that bromine-antimony and phosphorous-bromine combinations should be replaced with safer non-halogenated alternatives. A research group from Department of Polymer Chemistry at Åbo Akademi is working with an aim to produce novel non-halogenated flame retardants. First results of this research work show that azoalkanes could be an efficient non-halogenated family of flame retardants.

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