Multinuclear NMR Characterization of Ag(I) Perfluorinated Carboxylates Complexes with Bis(diphenylphosphino)methane

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Ag(I) perfluorinated carboxylate complexes with bis(diphenylphosphino)methane (dppm) of general formula \([\text{Ag}_2(\text{RCOO})_2(\text{dppm})]\), where R = CF₃, C₃F₇, C₄F₉, C₆F₁₃, C₉F₁₉ were synthesized and spectroscopically (\(^1\text{H}\), \(^1\text{C}\), \(^31\text{P}\), \(^1\text{F}\), NMR and IR) characterized. Temperature variable \(^31\text{P}\) NMR spectra were recorded and \(^3J_{(107\text{Ag}-31\text{P})}\), \(^3J_{(109\text{Ag}-31\text{P})}\), \(^3J_{(107\text{Ag}-1\text{P})}\), \(^3J_{(109\text{Ag}-1\text{P})}\) spin-spin coupling constants calculated. Analysis of coordination shifts and coupling constants are in favour of dimeric trigonal Ag(I) complexes with bridging carboxylates and dppm in solution. IR spectra suggest the same coordination mode in the solid state.


Potentiometric and Thermodynamic Studies of 3-(Trichlorophenylsulphonamido)rhodanine Complexes with Some Metal Ions

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Acid dissociation and complex stability constants of 3-(trichlorophenylsulphonamido)rhodanine (TCSR) with some metal ions were determined potentiometrically in 0.1 M KCl and 30% (v/v) ethanol-water mixture. The sequence of stability constants is: \(\text{Th}^{4+} > \text{UO}_{2}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}\). The dissociation constants \(pK_a\) of TCSR and the stability constants \(\log K\) of their complexes were determined at 298, 308 and 318 K. The corresponding thermodynamic parameters (DG, \(\Delta H\) and \(\Delta S\)) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavourable. The formation of the metal complexes has been found to be endothermic and entropically favourable.

New Polymeric Copper(II) Complexes with Triphenyl Phosphite and Perfluorinated Carboxylates

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New Cu(II) complexes with triphenyl phosphite and aliphatic perfluorinated carboxylates [Cu{P(OC₆H₅)₃}([CₓFₙ]-OH)({CₓFₙ}-RCOO)]ₙ, (where R = CF₃, C₂F₅, C₃F₇, C₆F₁₃, C₇F₁₅, C₈F₁₇, C₉F₁₉) were obtained and their spectroscopic and thermal properties studied. EPR spectra and magnetic susceptibility measurements indicate the formation of polymeric complexes. Examination of COO absorption bands suggests bridging carboxylates as well as a hydroxo group, whereas triphenyl phosphite is monodentately bonded. Thermal decomposition is a multistage process, which in nitrogen yields a mixture of Cu, Cu₂O and Cu₂P₂O₇, but in air – pure Cu₂P₂O₇.

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4-Azomalononitrile Antipyrine Complexes of Some First Row Transition Metals

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Fe(III), Co(II), Ni(II) and Cu(II) complexes of 4-azomalononitrile antipyrine (L) have been prepared in ethanol solution and characterized by IR, electronic, and ESR spectra as well as magnetic susceptibilities and molar conductivities. The ligand behaves as a neutral bidentate one and the coordination takes place via the azomethine nitrogen and the carbonyl oxygen atom. Ligand field parameters have been calculated and structures are proposed.
Copper(I) Nitrate \( \pi \)-Complexation:
Synthesis and Crystal Structure
of \([\{\text{CH}_2=\text{CH–CH}_2–\text{NHC(NH}_2\}_2\text{Cu(NO}_3\}_2]\) Compound

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By alternating-current electrochemical synthesis, a crystalline \( \pi \)-complex
\([\{\text{CH}_2=\text{CH–CH}_2–\text{NHC(NH}_2\}_2\text{Cu(NO}_3\}_2]\) (I) has been obtained using copper(II) nitrate
and allylguanidine (AGU) in butanol-2 solution and copper-wire electrodes. A single
crystal of the compound was X-ray structurally characterized. The Cu ion possesses
trigonal pyramidal coordination formed by two oxygen atoms of the two nitrate anions
and C=C bond of the \text{H}^+\text{AGU} cation at the equatorial plane and the oxygen atom of an-
other nitrate anion at the apical position. Owing to the bridging function of NO\(_3\)-group,
the structure I consists of chains connected by branched system of \((\text{N})\text{H...O}\) bonds of
2.19(4)–2.45(3) Å. New stereochemical features of coordinated nitrate anion in copper(I) \( \pi \)-complexes have been revealed.

New Coordination Compounds of Copper(II) with Guanidinopyrimidines in N,N-Dimethylformamide

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Several guanidinopyrimidine copper(II) complexes have been prepared in dimethyl-
formamide (DMF) and characterized by elemental analysis, electronic, EPR and vibra-
tional spectra and also by magnetic susceptibility measurements. The structure of the
nearest environment of the central ion has been determined. The general formula of the
complexes is Cu(N-C)L–X, where (N-C) is substituted guanidine, coordinated as a che-
lating ligand through the guanidinopyrimidine and a formal pseudoaromatic chelate ring
Cu–N bond; L = guanidinopyrimidine, X = ClO\(_4\).
Four new mixed complexes of Cu(II) with tpmc (N,N',N''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) and bridged bound N,S or N,O ligands of the general formula [Cu₂(X)tpmc](ClO₄)₄, where X = thiosemicarbazide (tsc), semicarbazide (sc), thiourea (tu) or urea (u), were prepared. Elemental and thermal analyses, conductometric and magnetic measurements, electronic, IR and mass spectroscopy have been employed. The molar conductivity values in acetonitrile show a behavior of 1:4 electrolytes. IR studies clearly indicate that X ligand is coordinated via N, S (tsc and tu) or N, O (sc and u) atoms, acting as bidentate bridging ligands. An exo coordination of Cu(II) ions and tpmc was proposed. Thermal decomposition of the complexes was performed. The mass decomposition pathways are proposed. Finally, the obtained complexes exhibit microbiological activity against some bacteria.

Further Investigations on the Optical Activity of Aromatic Residues in Cyclolinopeptide A Analogues

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CD spectra of a series of cyclolinopeptide A (CLA) analogues ([Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, [Ala₁]CLA, and [Ala₁]Phe(SO₃Na)₉][CLA]) in methanol solution were analyzed. It was confirmed that the aromatic residue in position 9 contributes to a low extent only to the optical activity of the

Dinuclear Copper(II) Complexes of N,N',N'',N'''-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane and Some N,S or N,O Bidentate Ligands

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peptide. However, this phenomenon is not a result of the “edge-to-face” interaction of aromatic side chains but rather of the conformation of the aromatic side chain in position 9. This conclusion is confirmed by the fact that the decrease of the optical activity in that position was also observed in the spectra of analogues with only one aromatic residue. Analysis of the CD spectra reveals also that, contrary to Leu¹, the Pro¹ residue of the fragment -Pro-Phe-Phe-Leu- is a factor that determines the conformation of the peptide backbone and, in the consequence, the conformation of aromatic residues.


**Synthesis of New Tetraoxacyclophanes Containing Benzophenone Units**

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4,4'-Dihydroxybenzophenone was used as a precursor for synthesis of macrocyclic compounds. Low-temperature crystal structures were determined for 4,4'-diethoxybenzophenone (10), C₁₇H₁₈O₃, orthorhombic, Phen, a = 7.2891(12), b = 6.2827(10), c = 31.1000(5) Å, Z = 4 (one molecule with twofold symmetry), and 1,5,19,23-tetraoxa-12,30-dioxo[5.1.5.1]paracyclophane (6), C₃₄H₃₂O₆, triclinic, P(-1), a = 9.1559(12), b = 11.634(2), c = 14.124(2) Å, α = 93.745(12), β = 102.966(10), γ = 108.591(12)°, Z = 2, (two independent molecules each with inversion symmetry). The interplanar angles between aromatic rings is 53° for compound 10 and 53°, 49° for the two molecules of 6. IR, Raman and UV spectra were recorded for both compounds.


**New Analogues of Proline-Rich Protein Fragments. Synthesis and Their Effect on Resistance of Murine Thymocytes to Hydrocortisone**

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New analogues of proline-rich protein (PRP) fragment were synthesized by the solid phase method using Boc/Bzl procedure. Dimer of the nonapeptide as well as dimer, trimer and tetramer of hexapeptide fragments of PRP possessing immunotropic activity were obtained. Effect of the peptides on the resistance of murine thymocytes to hydrocortisone was the same as that of the reference compounds (hexapeptide and nonapeptide).


Dimerization of Phenylindenes by Means of Perchloroalkanes Under Conditions of Phase Transfer Catalysis

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Phenyl substituted indenes 1 react with tetrachloromethane (2a) or hexachloroethane HCE (2b) in the presence of 50% aq. KOH and benzyltriethylammonium chloride (TEBAC) as a catalyst (phase-transfer catalysis, PTC) to give dimers 5 in 23–48% yield. These products are possibly formed via chlorination of carbanions 1+ with 2 to give 3, their deprotonation to chlorocarbanions 3−, alkylation with chloroindenes 3 to afford 4 and subsequent elimination of hydrogen chloride.


Methyl Esters of N-Protected-O- or -S-(4,6-di-O-acetyl-2,3-dideoxy-D-erythro-hex-2-enopyranosyl)-L-serine, -L-threonine and -L-cysteine: Synthesis and Some Transformations

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Methyl esters of N-tosyl-O-(4,6-di-O-acetyl-2,3-dideoxy-D-erythro-hex-2-enopyranosyl)-L-serine (5), -L-threonine (6) and N-benzoyl-S-(4,6-di-O-acetyl-2,3-dideoxy-f-D-erythro-hex-2-enopyranosyl)-L-cysteine (7) have been synthesized by condensation of 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol (1) with respective derivatives of L-serine (2), L-threonine (3) and L-cysteine (4). cis-Hydroxylation and epoxidation of 2,3-unsaturated glycopyranoside 5 afforded O-glycosyl-L-serine deriv-a-
tives with α-D-manno (8, 9), 2,3-anhydro-α-D-manno (10) and 2,3-anhydro-α-D-allo (11) structures, respectively. The structure of compounds as well as conformation of the sugar residue and configuration at the anomeric centre were established on the basis of the 1H and 13C NMR (DQF-COSY, TOCSY, HMBC), IR, MS (FD) spectrometric techniques and polarimetric data.


Modelling of Molecular and Chiral Recognition by Cyclodextrins. Is It Reliable? Part 2. Molecular Dynamics Calculations in Vacuum Pertaining to the Selective Complexation of Decalins by β-Cyclodextrin

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Mechanism and Kinetics of the Anodic Reaction in Cryolite Melts. II. The Influence of AlF3 (11 wt%) at Different Al2O3 Content

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Crystal Structure of N-Methylcamphorimide and Its Monothiocarbonyl and Monoselenocarbonyl Derivatives
Crystal structures of N-methylcamphorimide and its monothio and monoseleno analogues show pronounced non-planarity of the chromophore moieties. The observed degree of the chromophore deformation decreases on going from the N-methylcamphorimide through its thiocarbonyl to the selenocarbonyl analogue.


Synthesis and Properties of Thiocyanato-Bridged Chromium(III)–Copper(II) Hydroxo Complexes

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Copper(II) Methylpyrazole Complexes

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Crystal Structure of Morpholine Hydrofluoride Monohydrate

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Molecular and Crystal Structure of [Co(en)$_2$ox]SCN Having Spiral Strings

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Mechanism of the Acid Hydrolysis of
[Co(histamine)$_2$(CO$_3$)]$^+$ Complex Ion –
New Interpretation Based on a Factor Analysis Method

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