

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 $\text{R} = \text{CF}_3, \text{C}_3\text{F}_7, \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13}, \text{C}_9\text{F}_{19}$ were synthesized and spectroscopically (^1H , ^{13}C , ^{31}P , ^{19}F , NMR and IR) characterized. Temperature variable ^{31}P NMR spectra were recorded and $^1J(^{107}\text{Ag}-^{31}\text{P})$, $^3J(^{107}\text{Ag}-^{31}\text{P})$, $^1J(^{109}\text{Ag}-^{31}\text{P})$, $^3J(^{109}\text{Ag}-^{31}\text{P})$ 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^{H} of TCSR and the stability constants $\log K$ of their complexes were determined at 298, 308 and 318 K. The corresponding thermodynamic parameters (ΔG , ΔH and ΔS) 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 $[\text{Cu}\{\text{P}(\text{OC}_6\text{H}_5)_3\}(\mu\text{-OH})(\mu\text{-RCOO})]_n$, (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.

4-Azomalonitrile Antipyrine Complexes of Some First Row Transition Metals

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Fe(III), Co(II), Ni(II) and Cu(II) complexes of 4-azomalonitrile 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 π -Complexation: Synthesis and Crystal Structure of $[\{\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHC}(\text{NH}_2)_2\}\text{Cu}(\text{NO}_3)_2]$ Compound

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By alternating-current electrochemical synthesis, a crystalline π -complex $[\{\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHC}(\text{NH}_2)_2\}\text{Cu}(\text{NO}_3)_2]$ (**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 H^+AGU cation at the equatorial plane and the oxygen atom of another 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 (N)H...O bonds of 2.19(4)–2.45(3) Å. New stereochemical features of coordinated nitrate anion in copper(I) π -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 dimethylformamide (DMF) and characterized by elemental analysis, electronic, EPR and vibrational 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 $\text{Cu}(\text{N-C})\text{L-X}$, where (N-C) is substituted guanidine, coordinated as a chelating ligand through the guanidinopyrimidine and a formal pseudoaromatic chelate ring Cu–N bond; L = guanidinopyrimidine, X = ClO_4^- .

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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Four new mixed complexes of Cu(II) with *tpmc* (N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) and bridged bound N,S or N,O ligands of the general formula $[\text{Cu}_2(\text{X})\text{tpmc}](\text{ClO}_4)_4$, 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 ($[\text{Ala}^1]\text{CLA}$, $[\text{Ala}^7]\text{CLA}$, $[\text{Ala}^{1,7}]\text{CLA}$, $[\text{Ala}^8]\text{CLA}$, $[\text{Ala}^9]\text{CLA}$, $[\text{Ala}^8, \text{Tyr}^9]\text{CLA}$, $[\text{Ala}^9, \text{Tyr}^8]\text{CLA}$, and $[\text{Ala}^7, \text{Phe}(\text{SO}_3\text{Na})^9]\text{CLA}$) 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

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 Pro⁷ 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.

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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, *Pbcn*, $a = 7.2891(12)$, $b = 6.2827(10)$, $c = 31.1000(5)$ 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, $\alpha = 93.745(12)$, $\beta = 102.966(10)$, $\gamma = 108.591(12)^\circ$, $Z = 2$, (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.

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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).

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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.

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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- α -*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 epoxydation of 2,3-unsaturated glycopyranoside **5** afforded *O*-glycosyl-*L*-serine deriva-

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 ^{13}C NMR (DQF-COSY, TOCSY, HMBC), IR, MS (FD) spectrometric techniques and polarimetric data.

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**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 AlF_3 (11 wt%)
at Different Al_2O_3 Content**

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**Crystal Structure of N-Methylcamphorimide and Its
Monothiocarbonyl and Monoselenocarbonyl Derivatives**

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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.

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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)₂ox]SCN Having Spiral Strings

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Mechanism of the Acid Hydrolysis of [Co(histamine)₂(CO₃)⁺ Complex Ion – New Interpretation Based on a Factor Analysis Method

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