

Enantiomerically Pure Carbocyclic Derivatives from Sugar Allyltins

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(Received April 2nd, 2004; revised manuscript April 23rd, 2004)

The concise approach to enantiomerically pure, highly oxygenated carbocyclic derivatives from sugar allyltins as well as the preparation of these sugar organometallics is reviewed.

Synthesis, Characterization and Electrochemical Studies of Nickel(II) and Cobalt(II) Complexes with Novel Bidentate Salicylaldimines

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(Received December 23rd, 2003; revised manuscript March 4th, 2004)

Several mononuclear Ni(II) and Co(II) complexes of bidentate salicylaldimines (L_xH), derived from 3,5-di-tert-butyl-2-hydroxybenzaldehyde with biologically active amines [1-(3-aminopropyl)imidazole, 4-(3-aminopropyl)morpholine, 1-(3-aminopropyl)-2-pyrrolidinone], have been synthesized. The complexes have been characterized by FT-IR, UV-vis, MS, 1H -NMR and ^{13}C -NMR, magnetic susceptibility measurements, thermogravimetric analyses (TGA) and electrochemistry. As a result of thermal analyses, $Co(L_3)_2$ has highest thermal stability of the complexes, whereas the smallest one has $Ni(L_2)_2$. Electrochemical experiments indicated that Ni(II) and Co(II) complexes show quasi reversible reduction to Ni(I) and Co(I), respectively.

Syntheses, Structure and Magnetism of Heterobinuclear μ -Oxamido Cu(II)–Ni(II) Complexes Containing tacn as a Terminal Ligand

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(Received March 18th, 2004)

Two new heterobinuclear complexes, namely Ni(tacn)Cu(oxpn)(ClO₄)₂·2H₂O (**1**) and Ni(tacn)Cu(pmoxd)(ClO₄)₂·CH₃OH (**2**), have been prepared from the planar fragments Cu(oxpn) and Cu(pmoxd) (tacn denotes 1,4,7-triazacyclononane, oxpn and pmoxd stand for the dianions of *N,N'*-bis(3-aminopropyl)oxamide and *N,N'*-bis(2-pyridylmethyl)oxamide, respectively). Compound **1** crystallizes in the triclinic system, space group *P* $\bar{1}$, with $a = 8.573(2)$, $b = 12.808(3)$, $c = 13.122(3)$ Å, $\alpha = 99.63(3)$, $\beta = 104.72(3)$ and $\gamma = 96.45(3)^\circ$ at 299 K, $Z = 2$. The Cu(II) ions are in square-pyramidal surroundings and the Ni(II) ions in octahedral surroundings. The temperature dependence of the magnetic susceptibilities of **1** has been studied in the 5–300 K range, giving the exchange integral $J = -92.7$ cm⁻¹. This value, while close to those reported for other Cu(II)–Ni(II) complexes involving Cu(oxpn), represents the minimum exchange constant of such heterobinuclear system.

Synthesis, Spectroscopic and Thermal Studies of Vanadyl-N,N'-o-phenylenebis(salicylideneiminato) Complexes

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(Received November 24th, 2003; revised manuscript April 5th, 2004)

Two new complexes [V(O)(sal-o-phdn)(H₂O)] and [V(O)(sal-o-phdn)(C₂H₅OH)] (sal-o-phdn = N,N'-o-phenylenebis(salicylideneiminato)) have been synthesized and characterized by elemental and thermal analysis and electronic, infrared and Raman spectra. Both complexes are in the mononuclear forms where the Schiff base occupies the four equatorial positions and H₂O or C₂H₅OH are axially coordinated to the vanadyl oxygen forming distorted octahedral with C_s symmetry. The characteristic $\nu(\text{V}=\text{O})$ vibrations for the mononuclears are observed at 978 and 981 cm⁻¹ for the H₂O and C₂H₅OH complexes, respectively. Full vibrational assignments for all observed bands are made. The vibrations of the coordinated H₂O in [V(O)(sal-o-phdn)(H₂O)] are observed at 3255, 1704, 829 and 645 cm⁻¹ while those for the C₂H₅OH in [V(O)(sal-o-phdn)(C₂H₅OH)] are shown at 3620, 2950, 1386 and 860 cm⁻¹.

Studies on the Complexation of Alkali Metal Cations by Macrocyclic Diamides Using Electrospray Ionization Mass Spectrometry (ESI-MS)

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(Received April 5th, 2004; revised manuscript April 30th, 2004)

Several macrocyclic diamides have been tested as ligands for complexation of alkali metal cations. Electrospray ionization mass spectrometry was found to be a perfect tool for investigation of host-guest interaction between ligands and cations studied. Effect of the ring size and regioisomerism of the amido groups on complexation properties of ligands were also investigated.

Ethynylation of the Ether Derivatives of ω -Haloalkanols with Lithium Acetylide–Ethylenediamide Complex

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(Received March 22nd, 2004; revised manuscript April 26th, 2004)

A new operationally simple and highly efficient procedure for the ethynylation of ether derivatives of ω -haloalkanols with lithium acetylide–ethylenediamine complex in N,N-dimethylacetamide is described.

Convenient Synthesis of Phosphonate Derivatives of 4-Chloro-2*H*-chromenes

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(Received January 5th, 2004; revised manuscript May 4th, 2004)

2,4-Dichloro-2*H*-chromene-3-carboxylates are formed in good yield in the condensation of the appropriate precursors with SOCl₂. These derivatives readily react with trialkyl phosphites to produce 2-phosphonate derivatives of 4-chloro-2*H*-chromene-3-carboxylates.

Synthesis of HYNIC- and DOTA-Conjugates with μ -Opioid Receptor Ligands: Morphiceptin and Endomorphin-2

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(Received April 7th, 2004; revised manuscript May 11th, 2004)

Opioid peptides recently attracted much attention as low molecular weight compounds, which can target malignant cells expressing opioid receptors on their cell surface. Therefore opioid peptides have a potential to be introduced as radiopharmaceuticals. In this paper, we describe the method of conjugation of two bifunctional chelating agents (BFCAs), hydrazinopyridine-3-carboxylic acid (HYNIC) and 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA), to the N-terminal amino group of morphiceptin, endomorphin-2, and two of their analogs modified in position 3. GABA was used as a spacer molecule. μ -Opioid binding affinities of the peptides were compared with the binding affinities of BFCA-GABA-peptide conjugates. It was shown that the introduction of HYNIC to μ -opioid ligands causes only a slight decrease of μ -opioid receptor affinity, while DOTA-conjugates lose their affinity for μ -receptors completely.

Time-Resolved Emission Spectroscopy of Pyrene Derivatives

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(Received February 6th, 2004; revised manuscript April 15th, 2004)

An improved model of the picosecond time-resolved spectrofluorimeter equipped with an optical Kerr shutter was designed and constructed. The instrument was applied for measurements of time-resolved fluorescence (TRF) spectra of 4'-(pyrenyl-1-yl)acetophenone (Py-BK) and 4'-(pyrenyl-1-yl)benzotrile (Py-BN). The experimental results indicate that both molecules relax after excitation by mutual twisting of two subunits towards a more planar geometry. In the case of Py-BK the kinetics of creation of excited state hydrogen-bonded complexes was discussed in detail.

Perfluoroalkyl-*n*-eicosanes at the Air–Water Interface – A Monolayer Study

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(Received April 6th, 2004; revised manuscript May 5th, 2004)

Perfluoroalkyl-*n*-eicosanes of the general formula $F(CF_2)_m(CH_2)_{20}H$, where $m = 4, 6, 8, 10, 12$ were spread at the air/water as Langmuir monolayers and studied at different experimental conditions, such as spreading volume, subphase temperature and compression speed. The Langmuir monolayer experiments (π -*A* isotherms) have been complemented with quantitative Brewster angle microscopy results, which enabled estimation of the film thickness at different stages of compression. Although the investigated molecules do not possess any polar group and are purely hydrophobic, they form stable monomolecular layers at the free water surface. The negative sign of the measured surface potential, ΔV , evidences for the orientation of the molecules with their perfluorinated parts exposed towards the air, independently of the length of the perfluorinated moiety. The relative intensity measurements allow one to conclude that the molecules with shorter perfluorinated part (F4H20, F6H20 and F8H20) are oriented almost vertically (in respect to the interface) in the vicinity of film collapse, while F10H20 and F12H20 are tilted to the water surface.

Kinetics and Mechanism of Complex Formation between O-Bonded Pentaammine(valinato/prolinato)cobalt(III) Ions and Nickel(II) in Aqueous Medium

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(Received January 19th, 2004; revised manuscript May 7th, 2004)

The kinetics of reversible complexation of $\text{Ni}(\text{OH}_2)_6^{2+}$ with oxygen-bonded valinato/prolinatocobalt(III) substrates, $(\text{NH}_3)_5\text{Co}(\text{val/pro})^{3+}$ have been investigated by stopped flow technique at 25°C , $6.1 \leq \text{pH} \leq 6.70$ and $I = 0.3 \text{ mol dm}^{-3}$. The formation of binuclear species, $[(\text{NH}_3)_5\text{Co}(\text{val/pro})\text{Ni}]^{4+}$, occurred *via* the reaction of $\text{Ni}(\text{OH}_2)_6^{2+}$ with deprotonated (amine and imine functions of valine and proline, respectively) form of the cobalt(III) substrates, $(\text{NH}_3)_5\text{Co}(\text{val/pro})^{2+}$. The results indicate the formation of mono-bonded binuclear species through entry of the imine/amine functions into the coordination sphere of Ni(II) with Ni–OH₂ bond dissociation is limiting (I₄ mechanism). The binuclear species exist in dynamic equilibrium involving the mono-dentate and chelated forms with chelated forms predominating. The small values of dissociation rate constants, despite the intrinsic electrostatic repulsion between the like charge centers, also support the chelate nature of the binuclear species.

**Synthesis, Crystal Structure and Magnetic Behavior
of a Two-dimensional Cobalt(II) Complex with
Benzene-1,4-dinitro-2,3,5,6-tetracarboxylate
Tetravalent Anion as Bridging Ligand**

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(Received February 26th, 2004; revised manuscript May 10th, 2004)