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Dioxomolybdenum(VI) complexes of 3,5-dichlorosalicylidene-S-butyl-thiosemicarbazone

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Abstract: Thiosemicarbazones have been of great importance because of their biological activity. In recent years, many papers were published about structural properties and biological activity of metal complexes of thiosemicarbazone derivatives. However, studies of the thiosemicarbazone complexes with molybdenum as oligo element are in a relatively little number, and solvated molybdenum(VI) complexes of thiosemicarbazones, which are a special class of molybdenum chelates, are very limited. Various molybdenum complexes are essential in enzymes such as nitrogenase, sulfite, and xanthine oxidases, and even some of the molybdenum compounds are included in excellent enzyme model systems. In addition, it is known that some molybdenum compounds catalyze the oxygen atom transfer mechanisms.

Here in, two new dioxomolybdenum(VI) complexes were prepared with the reaction of dioxomolybdenum (VI) acetyl acetate and 3,5-dichlorosalicylaldehyde-4-ethyl-S-butyl thiosemicarbazone in ethanol or pyridine. The solid complexes were characterized by elemental analysis and spectroscopic methods.

Sažetak

Tiosemikarbazoni su od velikog značaja zbog svoje biološke aktivnosti. Poslednjih godina, objavljeni su mnogi radovi o strukturnim svojstvima i biološkoj aktivnosti metalnih kompleksa derivata tiosemikarbazona. Međutim, ograničen je broj studija koje se bave kompleksima tiosemikarbazona sa molibdenom kao oligo elemenatom i solvativanim kompleksima molibden (VI) tiosemikarbazona, koji su posebna klasa helata molibdena. Različiti kompleksi molibdena su od suštinskog značaja u enzimima: nitrogenaza, sulfid i ksantin oksidaze, a neki su kompleksi molibdena uključeni u sisteme prvoklasnih enzimskih modela. Osim toga, poznato je da neki spojevi molibdena kataliziraju mehanizme prijenosa atoma kisika. Pripremljena su dva nova dioksmolibden (VI) kompleksa reakcijom dioksmolibden (VI) acetalacetona i 3,5-dihlorosalicilaldehid-4-etil-S-butiltiosemickarbazona u etanolu ili piridinu. Čvrsti kompleksi su karakterizirani elementarnom analizom i spektroskopskim metodama.



3-ethoxysalicylaldehyde-4-ethyl-S-methyl-thiosemicarbazone and its Dioxomolybdenum(VI) complexes

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Abstract: The chemistry of thiosemicarbazones, mixed ligands, has attracted considerable interest primarily due to their biological activities. Those activities have been correlated with their metal-chelating abilities and reductive capacity. Also, such complexes are considered important because of their potential antibacterial, antiviral and antitumor activities. *cis*-dioxomolybdenum cation is present in the oxidized form of certain oxotransferase enzymes like xanthine oxidase/dehydrogenase, DMSO reductase, etc. This has created a tremendous impetus in synthesis of a number of model complexes mimicking the oxotransferase molybdoenzymes. In this study, 2 new solvate dioxomolybdenum(VI) complexes were obtained with the reaction of dioxomolybdenum(VI) acetyl acetate and 3-ethoxysalicylaldehyde-4-ethyl-S-methyl thiosemicarbazone with the use of as second ligand methanol or ethanol by known methods. Characterization of the compounds was explained by elemental analysis, IR, ¹H-NMR and UV-VIS spectroscopy methods.

Sažetak

Hemija tiosemikarbazona s mješovitim ligandima, privukla je značajan interes, prije svega zbog njihove biološke aktivnosti. Ove aktivnosti su u korelaciji sa njihovim sposobnostima za metal-helaciju i reduktivni kapacitet. Također, kao kompleksi smatraju se važnim zbog njihove potencijalne antibakterijske, antivirusne i antitumorske aktivnosti. Kation *cis*-dioksomolibdena prisutan je u oksidiranoj formi izvjesnih enzima oksotransferaze kao što su ksantin oksidaza/dehidrogenaza, DMSO reduktaza, itd. Ovo je potaklo sintezu brojnih modela kompleksa koje oponašaju moliboenzime oksotransferaze. Poznatom metodom dobijena su dva nova solvativana kompleksa dioksomolibdena (VI) reakcijom dioksomolibden (VI) acetilacetona i 3-etoksisalicilaldehid-4-etil-S-metiltiosemikarbazona uz upotrebu metanola ili etanola kao drugog liganda. Karakterizacija spojeva je objašnjena elementarnom analizom, IR, ¹H-NMR i UV-VIS spektroskopskim metodama.



Development of a New Amperometric Sensor for Dopamine Based on the Carbon Electrode Modified with Ru(III) Complex

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Ru(III) complexes,
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Dopamine,
Modified electrode,
Carbon ink,
Amperometry

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Abstract: Dopamine is one of the most important neurotransmitters controlling the motor activity, autonomic and endocrine functions as well as the mental and emotional health of the human being. On the one side, the reduced dopaminergic activity leads to Parkinson's disease, while on the other side, the increased dopaminergic activity is associated with the emergence of psychosis and schizophrenia. Considering the wide range of physiological and pathophysiological effects, the development of a new sensor for specific and selective measurement of dopamine at low levels of concentration can make a major contribution to the disease diagnosis. With the aim of developing a new dopamine amperometric sensor, a glassy-carbon electrode was modified. The electrode was modified with water-insoluble redox mediator Sodium bis [N-2-oxyphenyl-5-bromo-salicylideneiminato-*ONO*] ruthenate(III) complex using carbon ink. The electrode is scanned by Differential Pulse Voltammetry (DPV) and Cyclic Voltammetry (CV) in the range of -0.3 V to + 0.4 V vs. Ag/AgCl electrode in the phosphate buffer, pH 7.42. The modified electrode shows a fast electric current response, i.e. an excellent electro-catalytic activity for the oxidation of dopamine. Hydrodynamic (HA) and Flow injection (FIA) amperograms were also recorded. Amperometric measurements were performed at an applied potential of 0.0; 0.1 and 0.15 V. An impact from numerous interferences being present in real samples will be reduced by low working potential of this sensor.

Sažetak

Dopamin je jedan od najvažnijih neurotransmitera koji nadzire motoričke aktivnosti, autonomne i endokrine funkcije te mentalno i emocionalno zdravlje čovjeka. Snižena dopaminergična aktivnost, s jedne strane, dovodi do Parkinsonove bolesti, a s druge strane, povećana dopaminergična aktivnost povezuje se s pojavom psihoza i šizofrenije. S obzirom na širok raspon fizioloških i patofizioloških učinaka, razvoj novog senzora za specifično i selektivno mjerenje dopamina na niskim razinama koncentracije može dati veliki doprinos za dijagnozu bolesti. S ciljem razvoja novog amperometrijskog senzora za dopamin modificirana je elektroda od staklastog karbona. Elektroda je modificirana s ne topivim u vodi redoks medijatorom Natrij bis[N-2-oksifenil-5-bromosalicilideniminato-*ONO*] rutenat(III) kompleksom primjenom karbon tinte. Elektroda je skenirana diferencijalno pulsnom voltametrijom (DPV) i cikličnom voltametrijom (CV) u rasponu potencijala od -0.3 do 0.4 V prema Ag/AgCl elektrodi u fosfatnom puferu, pH 7.42. Modificirana elektroda pokazuje brz strujni odziv odnosno odličnu elektrokatalitičku aktivnost za oksidaciju dopamina. Također su snimljeni hidrodinamički i protočno-injekcioni amperogrami. Amperometrijska mjerenja su rađena na primijenjenom potencijalu 0.0; 0.1 i 0.15 V. Nizak radni potencijal senzora će smanjiti utjecaj brojnih interferenci prisutnih u realnim uzorcima.



Synthesis of dioxouranium(VI) complexes of S-propylthiosemicarbazones

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Keywords:

Thiosemicarbazones,
dioxouranium(VI),
Crystal structure,

Abstract: The condensation of an aldehyde or a ketone compounds with the hydrazine nitrogen atom of thiosemicarbazide has been known since 1900s. However, the amidic nitrogen of thiosemicarbazone does not react with these carbonyl compounds and coordinates to metal center. However, the amide nitrogen can be condensed with an aldehyde by transition metal ions having template effect in which metal center has the significant orientation effect. By this method, the structures obtained are metal complexes.

The alkylated thiosemicarbazones substituted on sulfur were synthesized using 5-bromosalicylaldehyde as starting material. The template reactions of the S-propylthiosemicarbazones in the presence of dioxouranium(VI) were investigated. Two dioxouranium(VI) complexes were synthesized. Propyl or allyl alcohol used as second ligand completed the seventh coordination site of $\text{UO}_2(\text{VI})$. The synthesized thiosemicarbazones and template complexes were characterized by elemental analysis, UV –visible, FTIR, and ^1H NMR. The structure of the dioxouranium(VI) complex, $[\text{UO}_2\text{L}(\text{allyl alcohol})]$, was studied by single-crystal diffraction. The uranium is seven-coordinate in a pentagonal-bipyramidal arrangement with two oxo groups occupying the apical positions..

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Sažetak

Kondenzacija aldehidnih ili ketonskih spojeva sa atomom hidrazinskog nitrogena iz tiosemikarbazida je poznata još od 1900-ih. Ipak, amidni nitrogen iz tiosemikarbazona ne reaguje sa ovim karbonilnim jedinjenjima i koordinira se na metalni centar. Međutim, amidni nitrogen može se kondenzirati sa nekim aldehidom uz pomoć jona prelaznog metala koji djeluje kao model u kojem metalni centar ima značajan orijentacioni efekt. Ovom metodom se dobijaju strukture metalnih kompleksa. Alkilirani tiosemikarbazoni supstituirani na sumporu, su sintetizirani iz 5-bromsalicilaldehida kao početnog reagensa. Ispitivane su templatne reakcije S-propiltiosemikarbazona u prisustvu dioksouranijuma (VI). Sintetizirana su dva kompleksa dioksouranijuma (VI). Propilni ili alilni alkohol koji je korišten kao drugi ligand zauzeo je sedmo koordinacijsko mjesto u $\text{UO}_2(\text{VI})$. Sintetizirani tiosemikarbazoni i templatni kompleksi su potvrđeni elementarnom analizom, UV–VIS, FTIR, i ^1H NMR. Monokristalnom difrakcijom određena je struktura kompleksa dioksouranijuma(VI), $[\text{UO}_2\text{L}(\text{alilalkohol})]$. Koordinacioni broj urana je sedam u strukturi pentagonalne bipiramide, sa dvije okso grupe na apikalnim pozicijama.



Synthesis and antioxidant activities of oxovanadium(IV) complexes of 3-hydroxy-S-methylthiosemicarbazones

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Keywords:

Thiosemicarbazones,
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CUPRAC

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Abstract: Thiosemicarbazones has a very broad range of biological properties as antiviral, antifungal, antibacterial, antitumor, anticarcinogenic and insulin mimetic properties. Biological properties of this class compounds depend on the substituent position, the metal centre and the oxidation number of the metal ion.

Antioxidants which are believed to reduce the risk of cancer have a great importance in these days. In addition, the uncontrolled production of free radical reactive oxygen species such as superoxide anion, hydroxyl radical, and hydrogen peroxide can induce DNA damage in humans.

Herein, we present two oxovanadium(IV) complexes with hydroxy substituted salicylaldehyde thiosemicarbazones in the ONNO coordination mode. All compounds were characterized using analytical and spectroscopic data. The free ligand and its metal complexes have been tested for *in vitro* antioxidant capacity by reduction of copper(II) neocuproine (Cu(II)-Nc) using the CUPRAC method. Furthermore, the antioxidant activity of the free ligand and its complexes were determined by *in vitro* methods measuring the scavenging activity of reactive oxygen species (ROS) including hydroxyl radical ($\cdot\text{OH}$), superoxide anion radical ($\text{O}_2^{\cdot-}$), and hydrogen peroxide (H_2O_2).

Sažetak

Tiosemikarbazoni imaju vrlo širok spektar bioloških svojstava kao što su: antivirusna, antifungalna, antibakterijska, antitumorska, antikancerogena i inzulin mimička svojstva. Biološka svojstva ove klase spojeva zavise od položaja supstituenta, metalnog centra i oksidacijskog broja metala. Antioksidansi za koje se vjeruje da smanjuju rizik od raka su sve od veće važnosti. Nekonolirano stvaranje slobodnih radikala reaktivnih oksigenovih vrsta, kao što su: superoksidni anion, hidroksilni radikal, i hidrogenperoksid mogu dovesti do oštećenja DNA kod ljudi. U ovom radu predstavljena su dva oksovanadium (IV) kompleksa s hidroksi supstituiranim salicilaldehid tiosemikarbazonima, ONNO koordinacijskim modelom. Svi spojevi su karakterizirani analitičkim i spektroskopskim podacima. Antioksidativni kapacitet slobodnog ligand i njegovog metalnog kompleksa su testirani *in vitro* redukcijom bakar (II) neokuproina (Cu (II)-NC) po CUPRAC metodi. Nadalje, antioksidativno djelovanje slobodnog liganda i njegovih kompleksa su određene *in vitro* metodom za mjerenje aktivnosti reaktivnih oksigenovih vrsta (ROS), uključujući hidroksilni radikal ($\cdot\text{OH}$), radikal superoksidnog aniona ($\text{O}_2^{\cdot-}$) i hidrogenperoksid (H_2O_2).

Spectroscopic evidence on interaction of ruthenates (III) derived from N-low alkyl-5-substituted salicylideneimine with calf thymus DNA

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Keywords:

ruthenium(III)
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intercalation
spectroscopic titration

Abstract: Interaction of Ru(III) complexes containing monobasic bidentate ON-donor Schiff base ligands derived from simple aliphatic amines with 5-substituted salicylaldehyde with calf thymus DNA has been studied using spectroscopic titration. Complexes of general formula $\text{Na}[\text{RuCl}_2(\text{N-R-5-X-salim})_2]$, where $\text{R} = \text{Pr, Et}$ and $\text{X} = \text{H, Cl, Br, NO}_2$, were prepared as previously reported by our group and purity was checked by infrared spectroscopy confirming expected composition. The intrinsic binding constants for CT DNA with eight complexes were determined by spectroscopic titration experiments giving surprising evidence of quite strong interaction with K_b values in range $(0.58\text{--}2.27) \times 10^4 \text{ M}^{-1}$, which could be result of moderate intercalation or strong groove binding. Results also showed that K_b values are more affected with change of substituent in position 5- on salicylaldehyde component of ligand then with change of amine suggesting that aldehyde component might have significant influence on binding of complex with CT DNA. Regardless to ammine component, K_b values decrease in order $\text{H} > \text{NO}_2 > \text{Br} \approx \text{Cl}$. Also, K_b values decrease with increasing alkyl chain of amine for the same substituent in position 5- of salicylideneimines.

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Sažetak

Interakcija Ru(III) kompleksa sa monobaznim bidentatnim ON-donorskim Schiff-ovim bazama izvedenim iz jednostavnih alifatskih amina i 5-supstituiranih salicilaldehida, sa calf thymus DNA ispitana je spektrofotometrijskom titracijom. Kompleksi opšte formule $\text{Na}[\text{RuCl}_2(\text{N-R-5-X-salim})_2]$, gdje je $\text{R} = \text{Pr, Et}$ i $\text{X} = \text{H, Cl, Br, NO}_2$ su pripremljeni po objavljenim procedurama, što je ranije izvijestila naša grupa, a čistoća je provjerena infracrvenom spektroskopijom potvrđujući očekivani sastav. Konstanta vezivanja CT DNA sa osam kompleksa je određena spektrofotometrijskom titracijom dajući iznenađujući rezultat umjereno jake interakcije sa K_b vrijednostima u području $(0.58 - 2.27) \times 10^4 \text{ M}^{-1}$, što je vjerovatno rezultat umjerene sposobnosti interkalacije ili jakog vezivanja u velikom žlijebu. Rezultati su također pokazali da je vrijednost K_b više afektirana sa promjenom supstituenta u poziciji 5- na salicilaldehidnoj komponenti liganda, nego sa promjenom amina sugerirajući da aldehidna komponenta može imati značajan uticaj na vezivanja kompleksa sa CT DNA. Bez obzira na aminsku komponentu K_b vrijednost pada u nizu $\text{H} > \text{NO}_2 > \text{Br} \approx \text{Cl}$. Također K_b vrijednost pada sa porastom alkinog lanca amina za isti supstituent u poziciji 5 salicilidenimina.



Synthesis and characterization of novel cationic complexes Ru(III) with N-heterocycles and Schiff base derived from salicylaldehyde

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Ruthenium, complex,
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salicylideneimine,
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Abstract: Ruthenium complexes are the subject of huge interest and imposing development in the last decades due to their many significant properties, especially anticancer and catalytic properties. Novel cationic complex compounds of Ru(III) with selected N-heterocycles and Schiff base derived from salicylaldehyde and aniline have been synthesized. The compounds with the general formula $[\text{RuB}_2(\text{N-Ph-salim})_2]\text{Cl}$ (where B = imidazole, pyrazole, indazole, pyrimidine and pyridine) were prepared from the reaction of Sodium dichloro-bis-[N-phenyl-salicylideneiminato-N,O]ruthenate(III) and selected N-heterocycles. The synthesis of the complexes was carried out in relative mild conditions by replacement of two easily outgoing chloride ions in starting compound with the heterocycle. Formulation and characterization of the new complexes were performed using MALDI-TOF/TOF mass spectrometry, FT-IR spectroscopy and UV/Vis spectrophotometry. In the octahedral environment of Ru(III), coordination of bidentate Schiff bases occurs through azomethine nitrogen and deprotonated phenolic oxygen while in heterocycles via nitrogen atoms. MALDI-TOF/TOF mass spectrometry confirmed existence of cations with general formula $[\text{RuB}_2(\text{N-Ph-salim})_2]^+$. Redox property of complexes has been determined by using cyclic voltammetry.

Sažetak

Zadnjih decenija kompleksi rutenija su predmet velikog interesa i imponantnog razvoja zbog njihovih mnogih značajnih osobina, među kojima se posebno ističu antikancerne i katalitičke osobine. Sintetizirani su novi kationski kompleksni spojevi Ru(III) sa odabranim N-Heterociklusima i Schiff-ovom bazom izvedenom iz saliciladehida i anilina. Spojevi opšte formule $[\text{RuB}_2(\text{N-Ph-salim})_2]\text{Cl}$ (gdje je B = imidazol, pirazol, indazol, pirimidin i piridin) pripremljeni su u reakciji između natrij dihloro-bis-[N-fenil-salicilideniminato-N,O]rutenata(III) i odabranog N - heterociklusa. Sinteza kompleksa provedena je u relativno umjerenim uslovima zamjenom dva lahko odlazeća hloridna jona iz polaznog spoja sa heterociklusom. Formulacija i karakterizacija novih kompleksa napravljena je na bazi MALDI-TOF/TOF masene spektrometrije, FT-IR spektroskopije i UV/Vis spektrofotometrije. U oktaedarskom okruženju Ru(III), koordinacija bidentatne Schiffove baze se ostvaruje preko azometinskog azota i deprotoniranog fenolnog kisika, dok se kod heterociklusa ostvaruje preko atoma azota. MALDI-TOF/TOF masena spektrometrija potvrdila je postojanje kationa opšte formule $[\text{RuB}_2(\text{N-Ph-salim})_2]^+$. Redoks osobine kompleksa određene su cikličnom voltametrijom.



Spectrophotometric determination of binding constants of Ru(III) salicylideneimine complexes with CT DNA

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Keywords:

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 CT DNA
 intercalation
 spectroscopic titration
 salicylideneimine

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Abstract: Ruthenium as a coordination center in different complexes is interesting due to many reasons, especially because its complexes act as catalysts, electron-transfer mediators or anticancer agents depending on a coordination environment. Schiff's bases are organic ligands that have many good properties that qualify them in development and design of novel metal complexes. That is due to their antibacterial, antiviral and anticancer activity, significant stereochemical flexibility, and possibility to tune the electrode potential of metal complex. Here, we are giving report about interaction of eleven Ru(III) salicylideneimine complexes with general formula $\text{Na}[\text{Ru}(\text{N-R-5-X-salim})_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{O}$, $\text{X} = \text{H, Cl, Br, NO}_2$), $\text{Na}[\text{RuCl}_2(\text{N-R-5-X-salim})_2]$ ($\text{R} = \text{C}_4\text{H}_9$, $\text{X} = \text{H, Cl, Br, NO}_2$) and $[\text{Ru}(\text{N-R-5-X-salim})_3]$ ($\text{R} = \text{C}_{10}\text{H}_7$, $\text{X} = \text{H, Cl, Br}$) with CT DNA. Spectrophotometric titrations were used for quantification of complex interaction with DNA. Experimental data show that Ru(III) complexes with salicylideneimine act as moderate intercalators of CT DNA with binding constant of 10^4 M^{-1} magnitude. There is an evident influence of substituent in position 5 in salicylaldehyde on binding constants values.

Sažetak

Rutenij kao centar koordinacije u raznim kompleksima je interesantan iz više razloga, a posebno zbog sposobnosti rutenijskih kompleksa da u najrazličitijim koordinacionim okruženjima djeluju kao katalizatori, elektron-transfer medijatori ili antikanceri. Schiff-ove baze su organski ligandi koji imaju niz osobina koje ih kvalificiraju u razvoju i dizajnu novih metalnih kompleksa, od kojih su posebno značajne njihovo antibakterijsko, antiviralno i antitumorno djelovanje, te velika stereohemijska fleksibilnost i mogućnost podešavanja elektrodnog potencijala metalnog kompleksa. U ovom radu se izvještava o interakciji 11 salicilideniminskih kompleksa Ru(III) sa calf thymus DNA, opštih formula $\text{Na}[\text{Ru}(\text{N-R-5-X-salim})_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{O}$, $\text{X} = \text{H, Cl, Br, NO}_2$), $\text{Na}[\text{RuCl}_2(\text{N-R-5-X-salim})_2]$ ($\text{R} = \text{C}_4\text{H}_9$, $\text{X} = \text{H, Cl, Br, NO}_2$) i $[\text{Ru}(\text{N-R-5-X-salim})_3]$ ($\text{R} = \text{C}_{10}\text{H}_7$, $\text{X} = \text{H, Cl, Br}$). Za kvantifikaciju interakcije kompleksa sa CT DNA korištena je spektrofotometrijska titracija. Eksperimentalni podaci pokazuju da ispitivani salicilideniminski kompleksi Ru(III) nastupaju kao umjereni interkalatori CT DNA sa konstantama vezivanja reda veličine 10^4 M^{-1} . Evidentan je uticaj supstituenta u poziciji 5 na salicilaldehidnoj komponenti na vrijednost konstante vezivanja.



Mixed ligand complex of dioxomolybdenum(VI) 3-methoxy-salicylaldehyde-S-propyl-thiosemicarbazone and 3-methyl-2-butene-1-ol

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Crystal structure

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Abstract: Molybdenum is an oligo-element and one of cofactors for several enzymes catalysing redox reactions and some molybdenum compounds are included in plausible enzyme model systems. The known molybdenum (VI) complexes of thiosemicarbazones of general formula $[\text{MoO}_2\text{L}(\text{L}')]$ are potential catalysts as the coordinated L' molecule may be replaced by the activated enzyme molecule.

New dioxomolybdenum(VI) complex was prepared by reaction of 3-methoxysalicylaldehyde S-propyl-thiosemicarbazone (L) with $[\text{MoO}_2(\text{acac})_2]$ in 3-methyl-2-butene-1-ol (L'). In the complex, the doubly deprotonated ligand is coordinated to molybdenum through tridentate ONN-donor set consisting of phenolic oxygen, azomethine nitrogen and thioamide nitrogen. The solid complex of general formula $[\text{MoO}_2\text{L}(\text{L}')]$ which contain 3-methyl-2-butene-1-ol (L') as second ligand was characterized by elemental analysis and spectroscopic methods. The structure of the complex was determined by the single crystal X-ray diffraction method. X-ray crystal studies indicated a distorted octahedral geometry for complex. The MoO_2 unit has a *cis*-dioxomolybdenum structure with angles ca. 105° .

Sažetak

Molibden je oligo-element, on je kofaktor u nekim enzimski kataliziranim redoks reakcijama neki od spojeva molibdena su uključeni u enzimski sistem. Poznati kompleksi molibden (VI) tiosemikarbazona opće formule $[\text{MoO}_2\text{L}(\text{L}')]$ su potencijalni katalizatori jer koordinirana L' molekula može biti zamijenjena aktiviranom molekulom enzima. Novi kompleks dioksmolibdena (VI) je pripremljen reakcijom 3-metoksisalicilaldehid S-propil-tiosemikarbazona (L) sa $[\text{MoO}_2(\text{acac})_2]$ u 3-metil-2-buten-1-ol (L'). U kompleksu, dvostruko deprotonirani ligand je koordiniran na molibden preko tridentatnog ONN-donorskog seta koji se sastoji od fenolnog oksigena, azometinskog nitrogena i tioamidnog nitrogena. Čvrsti kompleks opće formule $[\text{MoO}_2\text{L}(\text{L}')]$ koji sadrži 3-metil-2-buten-1-ol (L') kao drugi ligand, karakteriziran je elementarnom analizom i spektroskopskim metodama. Struktura kompleksa je određena metodom difrakcije monokristala X-zracima. Rezultati su pokazali narušenu oktaedarsku geometriju kompleksa. MoO_2 ima strukturu *cis*-dioksmolibdena s uglovima oko. 105° .



***cis*-Dioxomolybdenum(VI) complexes with N-pentyl-thiosemicarbazone of 2-hydroxy-3-methoxy-benzaldehyde**

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Keywords:

Thiosemicarbazone
ONS ligand
Dioxomolybdenum complex
Structural analysis

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Abstract: Some molybdenum compounds have biological effects including cofactors for several enzymes such as nitrogenase, sulfite and xanthine oxidases catalyzing redox reactions. Catalytic capacity of the molybdenum compounds has been thought to be related with structural features of coordinated *cis*-MoO₂ unit, chelate ring structure and also substituents of ligands. Besides, some *cis*-dioxomolybdenum(VI) complexes may be catalyst for oxygen atom transfer mechanisms. Thiosemicarbazones have a wide range of pharmacological activity due to their ability to chelate with trace metals, and therefore dioxomolybdenum(VI)-thiosemicarbazone complexes have raised considerable interest. In this study, two *cis*-MoO₂²⁺ complexes having the general formula [MoO₂(L)(L')] were synthesized. In the complexes, L is dianionic form of 2-hydroxy-3-methoxy-benzaldehyde -N⁴-pentylthiosemicarbazone (H₂L) and L' are methanol or ethanol. Characterizations of the compounds were carried out by elemental analysis, electronic, infrared and ¹H-NMR spectroscopies. The ligand is coordinated to the *cis*-MoO₂²⁺ unit through O, N and S atoms which are phenolic oxygen, azomethine nitrogen and thiolate sulphure, respectively. The sixth coordination site of *cis*-MoO₂²⁺ is occupied by oxygen of alcohol.

Sažetak

Neki spojevi molibdena imaju biološke efekte, oni su kofaktori za neke enzime kao što su: nitrogenaze, sulfit i ksantin oksidaze koji kataliziraju redoks reakcije. Smatra se da je katalitički kapacitet spojeva molibdena u vezi sa strukturnim karakteristikama koordiniranog *cis*-MoO₂, strukturom helatanog prstena kao i supstituentima na ligandima. Osim toga, neki kompleksi *cis*-dioksomolibdena (VI) mogu katalizirati mehanizme prenosa oksigena. Kompleksi tiosemikarbazona su sve interesantniji jer imaju širok spektar farmakološke aktivnosti zbog svoje sposobnosti da se heliraju sa metalima u tragovima.

Ovdje su sintetizirana dva nova kompleksa *cis*-MoO₂²⁺ opće formule [MoO₂(L)(L')]. U kompleksima, L je dianionski oblik 2-hidroksi-3-metoksi-benzaldehid-N⁴-pentiltiosemikarbazona (H₂L) a L' je metanol ili etanol. Spojevi su karakterizirani elementarnom analizom, elektronskom, infracrvenom i ¹H-NMR spektroskopijom. Ligand je koordiniran na *cis*-MoO₂²⁺ preko atoma O, N i S koji redom pripadaju fenolu, azometinu i tiolatu. Šesto koordinacijsko mjesto na *cis*-MoO₂²⁺ zauzima oksigen iz alkohola.



Nickel(II)-Triphenylphosphine complex of S-methyl, N⁴-methyl substituted thiosemicarbazone

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Keywords:

Schiff base
Nickel complex
Triphenylphosphine
X-ray crystal structure

Abstract: Thiosemicarbazones are an important class of Schiff base ligands known for their selectivity and sensitivity towards various metal ions. In addition to antitumor effect of transition metal complexes of thiosemicarbazones, it is well known that they are also antiviral, even anti-HIV chemicals.

The study presents new nickel(II) complex obtained by reaction of $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ with 5-Bromo-2-hydroxy-S-methyl- N-methyl benzaldehyde thiosemicarbazone (H_2L). Elemental analysis, IR, UV-vis and $^1\text{H-NMR}$ spectrum have been used to characterization of the thiosemicarbazone ligand and nickel phosphine complex. The structure of $[\text{NiL}(\text{PPh}_3)]$ the complex was also determined by single crystal X-ray diffraction. Crystal study of the nickel complex with S-methyl-N⁴-methyl substituted thiosemicarbazidato ligand was reported for the first time.

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Sažetak

Tiosemikarbazoni su važna klasa liganda Schiffovih baza, poznatih po selektivnosti i osjetljivosti ka različitim metalnim jonima. Kao dodatak antitumornom efektu kompleksa prelaznih metala sa tiosemikarbazonom, dobro je poznato da imaju antivirusne, čak i anti-HIV osobine.

U ovom radu prikazani su novi nikel (II) kompleksi dobiveni u reakciji $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ sa 5-brom-2-hidroksi-S-metil- N-metil benzaldehid tiosemikarbazonom (H_2L). Elementarna analiza, IR, UV-vis i $^1\text{H-NMR}$ spektri su snimljeni za karakterizaciju tiosemikarbazonskih liganada i nikel fosfinskih kompleksa. Struktura $[\text{NiL}(\text{PPh}_3)]$ kompleksa je također potvrđena metodom difrakcije monokristala X-zrakama. Po prvi put je objavljeno istraživanje nikel kompleksa sa S-metil-N⁴-metil supstituisanim tiosemikarbazidat ligandima.

3-Bromo-5-chloro-acetophenone-N-hexyl-thiosemicarbazidato triphenylphosphine nickel(II) complex

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Keywords:

Thiosemicarbazone
Nickel complex
Triphenylphosphine
Structural analysis

Abstract: For many years, thiosemicarbazones and their metal complexes have been the subject of most structural and medicinal studies because of biological significance and phosphine ligands are reactive and versatile homogeneous catalysts in reactions, also. By study, $[\text{NiL}(\text{PPh}_3)]$ complex was synthesized by reaction of $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ with 3-bromo-5-chloro-2-hydroxyacetophenone-N-hexyl-thiosemicarbazone (H_2L). Thiosemicarbazone ligand and nickel phosphine complex was characterized by elemental analysis, IR and ^1H -NMR spectrum and the complex was also determined by single crystal X-ray diffraction.

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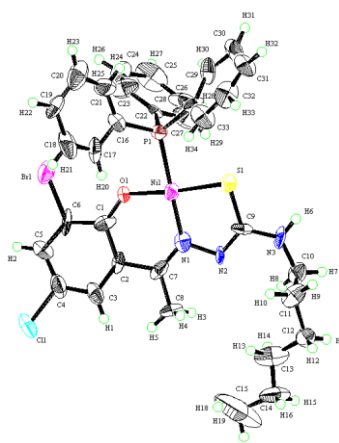
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Sažetak

Dugi niz godina, tiosemikarbazoni i njihovi metalni kompleksi su bili predmet većine strukturnih i medicinskih istraživanja zbog njihovog biološkog značaja, a fosfin ligandi su reaktivni i raznovrsni homogeni katalizatori u reakcijama.

U ovom radu, $[\text{NiL}(\text{PPh}_3)]$ kompleks je sintetizovan u reakciji $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ sa 3-brom-5-hlor-2-hidroksiacetofenon-N-heksil-tiosemikarbazonom (H_2L). Tiosemikarbazonski ligand i nikel fosfinski kompleks su okarakterizirani elementarnom analizom, IR i ^1H -NMR spektrima, a kompleks je potvrđen metodom difrakcije monokristala X-zrakama.





Synthesis and Characterization of a New Thiocarbohydrazone and its Dioxomolybdenum (VI) Complex

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Keywords:

Schiff base
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Thiocarbohydrazone
Dioxomolybdenum(VI) complex

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Abstract: Chemistry of the mixed hard-soft nitrogen-sulfur chelating ligands bound to Mo at higher oxidation state is a field of current interest. Such studies did assume greater importance after the revelation that several oxido-reductases like DMSO reductase, xanthine oxidase and other oxo-transferases contain Mo(IV), Mo(V) and Mo(VI) as their prosthetic groups coordinated to nitrogen-sulfur donor points of a macromolecular ligand system. Thiocarbohydrazones and their transition metal complexes are generally screened for antibacterial and antifungal activity using the bacteria *Azotobacter* and *Rhizobium* and the fungus *Fusarium oxysporium*. Thiocarbohydrazone ligand (H_3L) was obtained by the condensation of thiocarbohydrazide with 3,5-dibromo salicylaldehyde. Also, solvate dioxomolybdenum(VI) complex of general formula $[MoO_2(HL)(Metanol)(DMF)]$ were prepared in methanol + DMF. The structure of thiocarbohydrazone ligand and its oxomolybdenum(VI) complex have been characterized by elemental analysis, IR, 1H -NMR, UV-VIS spectroscopic techniques and thermogravimetric analysis.

Sažetak

Hemija mješanih tvrdo-mekih nitrogen-sumpor helatirajućih liganada, koji se vežu za Mo u višim oksidacionim stanjima je područje trenutnog interesa istraživanja. Takva istraživanja su pokazala značajnu važnost, nakon otkrivanja nekoliko oksido-reduktaza kao DMSO reduktaza, ksantin oksidaza i druge okso-transferaze koje sadrže Mo (IV), Mo (V) and Mo (VI), pošto su njihove prostetičke grupe koordinirane na nitrogen-sumpor donorska mjesta u makromolekularnom ligandnom sistemu.

Tiokarbohidrazoni i njihovi kompleksi sa prelaznim metalima se općenito proučavaju zbog antibakterijskih i antigljivičnih svojstava bakterija *Azotobacter* i *Rhizobium*, te gljivica *Fusarium oxysporium*.

Tiokarbohidrazon ligand (H_3L) je dobiven u reakciji kondenzacije tiokarbohidrazida sa 3,5-dibrom salicilaldehidom. Također, solvati dioksoomolibden (VI) kompleksa opće formule $[MoO_2(HL)(Metanol)(DMF)]$ su pripremljeni u metanol + DMF smjesi. Struktura tiokarbohidrazon liganada i njihovih oksomolibden (VI) kompleksa je okarakterizirana elementarnom analizom, IR, 1H -NMR, UV-VIS spektroskopskim tehnikama i termogravimetrijskom analizom.