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ANALYSIS OF QUANTUM-CHEMICAL AND IR-SPECTRA OF COORDINATION COMPOUNDS OF Cu(II), Cd(II), Co(II) SALTS WITH 2-AMINOBENZOXAZOLE

Annotation

According to the results of the analysis of the scientific literature, there is little information about the complexes formed by metals with 2-aminobenzoxazole and their properties. Methods of synthesis of metal complex compounds of Cu(II), Cd(II) and Co(II) of acetates with 2-aminobenzoxazole were developed and metallic complex compounds were synthesized using these methods. Composition, structure of synthesized complex compounds modern physico-chemical methods; was analyzed using elemental analysis, IR-spectroscopy analysis. It was found that the ligand 2-aminobenzoxazole is coordinated through the nitrogen atom in the benzoxazole ring during complex formation reactions.

Key words: Aminobenzoxazole, electron donor atom, ligand, infrared spectroscopy, monodentant, elemental analysis, quantum chemical calculation.

АНАЛИЗ КВАНТОВО-ХИМИЧЕСКИХ И ИК-СПЕКТРОВ КООРДИНАЦИОННЫХ СОЕДИНЕНИЙ СОЛИ Cu(II), Cd(II), Co(II) С 2-АМИНОБЕНЗОКСАЗОЛОМ

Аннотация

По результатам анализа научной литературы мало информации о комплексах металлов с 2-аминобензоксазолом и их свойствах. Разработаны методы синтеза металлокомплексов ацетатов Cu(II), Cd(II) и Co(II) с 2-аминобензоксазолом и с их помощью синтезированы металлокомплексы. Состав, структура синтезированных комплексных соединений современными физико-химическими методами; анализировали с помощью элементного анализа, ИК-спектроскопического анализа. Установлено, что лиганд 2-аминобензоксазол координируется через атом азота в бензоксазольном кольце в ходе реакций комплексообразования.

Ключевые слова: Аминобензоксазол, электронодонорный атом, лиганд, инфракрасная спектроскопия, монодентант, элементный анализ, квантово-химический расчет.

Cu(II), Cd(II), Co(II) TUZLARINING 2-AMINOBENZOKSAZOL BILAN KOORDINASION BIRIKMALARINING KAVANT-KIMYOVIY VA IQ-SPEKTRLARI TAHLILI

Annotatsiya

Ilmiy adabiyotlarning tahlil natijalariga ko‘ra metallarning 2-aminobenzoksazol bilan hosil qilgan komplesklari va ularning xossalari haqida ma’lumot kam keltirilgan. Cu(II), Cd(II) va Co(II) atsetatlarining 2- aminobenzoksazol bilan metall kompleks birikmalarini sintez usullari ishlab chiqildi va shu usullar yordamida metallik kompleks birikmalar sintez qilindi. Sintez qilingan kompleks birikmalarning tarkibi, tuzilishi zamonaviy fizik-kimyoviy usullar; element analizi, IQ-spektroskopiyasi analizlari yordamida tahlil qilindi. Ligand 2- aminobenzoksazol kompleks hosil bo‘lish reaksiyalarida benzoksazol halqasidagi azot atomi orqali koordinatsiyaga uchrashi aniqlandi.

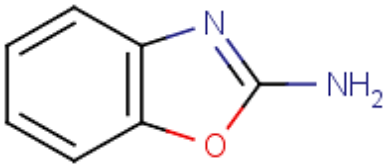
Kalit so‘zlar: Aminobenzoksazol, elektrodonor atom, ligand, infraqizil-spektroskopiyasi, monodentant, element analiz, kvant-kimyoviy hisoblash.

Kirish. Ma’lumki, biologik faol bo‘lgan organik birikmalar tarkibida biometallarni kiritilishi ularni nafaqat zararli tomonlarini kamaytiribgina qolmasdan balki, ko‘pgina hollarda biologik faolligini oshiradi yoki yangi biologik xususiyatlarni namoyon qiladi. Shuning uchun yangi, yuqori effektli biopreparatlarni sintezlash va ularni zamonaviy usullar yordamida o‘rganish hozirgi kunda dolzarb hisoblanadi.

Hozirgi kunda biologik faol bo‘lgan, tuzilishi va xossalari jihatidan katta farq qiladigan, o‘zida elektrodonor atomlar tutgan hamda koordinatsion birikmalar hosil qilishga moyil bo‘lgan ko‘plab organik va noorganik ligandlar mavjud bo‘lib, ularning eng muhim sinflaridan biri benzoksazol va uning hosilalari hisoblanadi[1].

Benzoksazol asosidagi fiziologik faol birikmalar molekulasida elektrofil va elektrofob reaksion markazlar bilan kuchli qutblangan guruhlar hosil bo‘ladi va bu bilan ular biologik faollikni namoyon etib, fermentlar yoki boshqa hujayralarni o‘rab olish uchun dastlabki reagent vazifasini o‘taydi. Bu esa, ma’lum tuzilish va xususiyatli koordinasion birikmalarni maqsadli sintez qilishga imkon beradi [2].

2-Aminobenzoksazol (1-rasm), IUPAC nomi 1,3-benzoksazol-2-amin, yalpi formulasi C7H6N2O suvda va boshqa qutbli erituvchilarda eriydigan rangsiz qattiq moddadir. Molyar massasi 134 g/mol, erish temreraturasi 129OC. Ko‘pgina murakkab molekulalarni sintez qilishda muhim oraliq mahsulot bo‘lib, farmatsevtika, bo‘yoq va boshqa birikmalar ishlab chiqarishda qo‘llaniladi.



1-rasm. 2-aminobenzoksazol

2-aminobenzoksazollar va ularning o‘rnini bosuvchi analoglari turli kasalliklar uchun potentsial dori nomzodlari sifatida tavsiflangan: irritabiy ichak sindromi [3], Altsgeymer kasalligi [4], uyqusizlik [5], surunkali obstruktiv o‘pka kasalligi kabi kognitiv disfunktsiyani davolash uchun. (RDE ingibitori 4) [6], geratit C [7], OIV va yallig‘lanish kasalliklaridan [8].

2-aminobenzoksazollar proteazlar, ximaza , butirilxolinesteraza , toroizomeraz II va boshqalarning ingibitorlari sifatida tavsiflangan [9], materiallar kimyosida qo‘llaniladi [11] va shuningdek, rozitron emissiya tomografiyasi uchun zondlar sifatida xizmat qiladi [12].

2-aminobenzoksazol bo‘yicha ko‘plab kelajakdagi tadqiqot yo‘nalishlari mavjud. Bularga uning biokimyoviy va fiziologik ta'sirini yanada o‘rganish, yangi sintez usullarini ishlab chiqish va dori vositalarini kashf qilish va ishlab chiqish uchun potentsial qo‘llanilishini tekshirish kiradi. Bundan tashqari, uning organik sintezda katalizator sifatida, koordinatsion kimyoda ligand sifatida va geterotsiklik birikmalar sintezida qurilish bloki sifatida qo‘llanilishi bo‘yicha keyingi tadqiqotlar o‘tkazilishi mumkin. Nihoyat, analitik kimyoda biologik marker sifatida potentsial foydalanish bo‘yicha keyingi tadqiqotlar o‘tkazilishi mumkin.

Asosiy qism. Komplesk birikmani sintez qilish uchun metallarning atsetatli va xloridli tuzlaridan foydalanildi.

Kompleks birikmalarning sintezi. Cu2(L)(CH3COO)4.H2O kompleks birikmasini sintez qilish uchun 2 mol 2-aminookzazolni 10ml spirtdagi eritmasiga 1 mol Cu(CH3COO)2.4H2O tuzining suvdagi eritmasidan tomchilatib qo‘shildi. Reaksion aralashma 30 minut suv hammomida aralashtirib turgan holda qizdirildi. So‘ngra sovutish uchun qoldirildi.

Hosil bo‘lgan pushti rangli cho‘kma dastlab ochiq havoda, so‘ngra 400C gacha qurutish pechida massasi o‘zgarmay qolgunga qadar qurutildi. Mahsulot unumi – 90,2%, Tsuyuq.= 2100C.

Co2(L)(CH3COO)4.H2O va Cd4L2Cl2 kompleks birikmalari ham yuqorida bayon etilgan usul bo‘yicha sintez qilib olindi. Och yashil rangli Co2(L)(CH3COO)4.H2O kompleks birikmasining reaksiya unumi – 72,9%, Tsuyuq.= 2200C.

To‘q yashil rangli Cd2(L)(CH3COO)4.H2O kompleks birikmasining reaksiya unumi – 83,8%, Tsuyuq.= 2500C.

Olingan kompleks birikmalarning element analiz natijalari

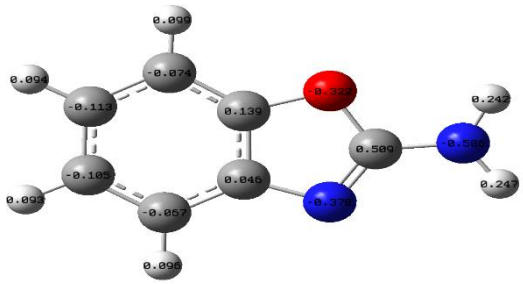
1- jadval

Sintez qilingan kompleks birikmalarning element analizi natijalari o‘rganildi:

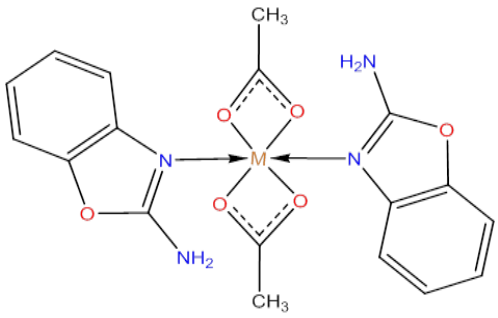
Birikma	Reaksiya unumi %	$T_{Suyuq.}$ ^0C	Ranggi	Topilgan / hisoblangan, %				
				C	H	O	N	Me
L	95	129	Oq	68,00 67,90	6,90 6,80	9,10 8,90	16,01 15,90	-
$Cu_2(L)(CH_3COO)_4{\cdot}H_2O$	90,2	210	Pushti	30,83 30,8	3,64 3,81	34,26 34,35	5,99 5,95	25,25 28,09
$Co_2(L)(CH_3COO)_4{\cdot}H_2O$	72,9	220	Och yashil	30,19 30,18	3,56 3,58	33,54 33,56	5,87 5,86	26,83 26,84
$Cd_2(L)(CH_3COO)_4{\cdot}H_2O$	83,8	250	To‘q yashil	19,96 19,95	1,25 1,25	6,65 6,66	11,64 11,65	45,74 45,73

Element analizi natijalaridan Me:L=2:1 nisbatda ekanligini ko‘rish mumkin.

2-aminobenzoksazolning IQ-Fure spektrlari 4 cm-1 tasvirli DTGS detektor bilan jihozlangan Nicolet iS10 IQ-Fure spektrometri yordamida xona haroratida KBr tabletkalari ko‘rinishida yozib olindi. Asosiy holatda 2-aminobenzoksazol molekulyar strukturaci 6-311G (d,r) bazac to‘plamiga ega B3LYR dasturining Gaussian 09 platformasida optimallashtirildi, bu o‘z navbatida Li-Yang-Parr korrelyatsion funksionaliga ega uch parametrli almashinuvchan Bekes funksionali gibridi hisoblanadi. 2-aminobenzoksazolning tebranuvchi chastotalari B3LYR darajasida hisoblandi. (RED) Potensial energiyani taqsimlanishini VEDA 4 (Vibrational Energy Distribution Analysis) (Tebranuvchi energiyani taqsimlanish analizi) dasturi yordamida hisoblandi. Masshtabli koeffitsientlarni hisoblash usuli Skot hamda Radom tomonidan tavsiya etilgan usul bilan bir xil.

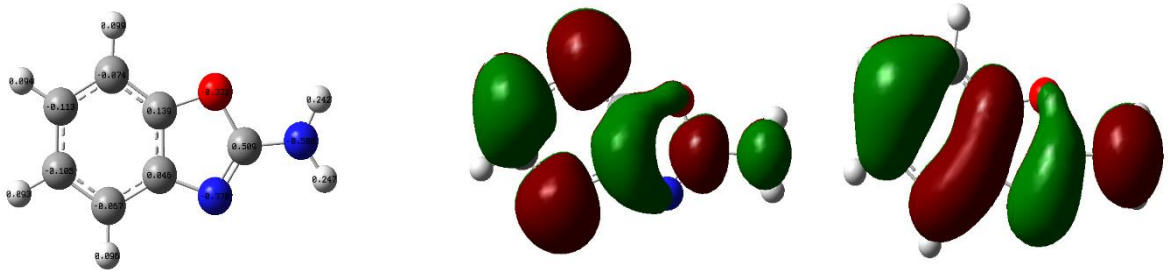


2-rasm. 2-aminobenzoksazolning molekulyar strukturasi va atomlarining raqamlanishi.



3-rasm. 2-aminobenzoksazolning metallar bilan hosil qilgan kompleksi

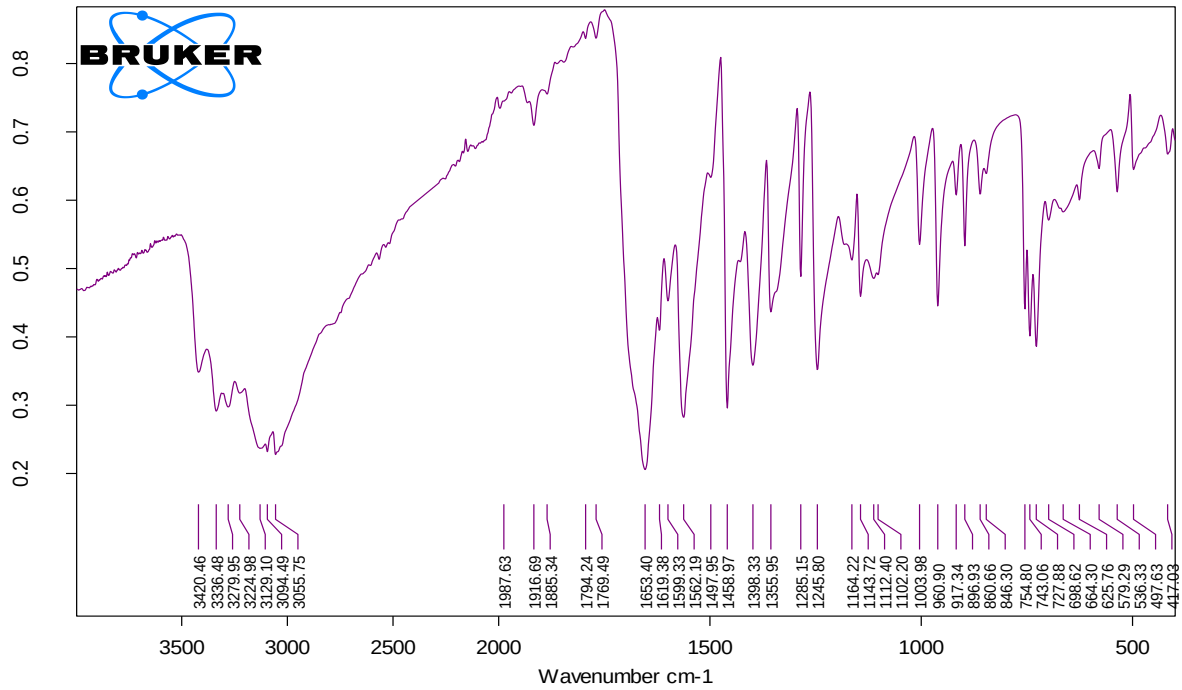
Ushbu usul yordamida tautomer formalar geometriyasi optimallashtirildi va umumiy energiyalar (Et), chegaraviy molekulyar orbitallar (MO) energiyasi va chegaraviy MO (ΔE) o‘rtasidagi energetik farqlar hisoblandi. Shuningdek, atomlardagi umumiy zaryadlar taqsimoti hamda yuqori band MO (YUBMO) zaryadning taqsimlanishi hisoblandi.



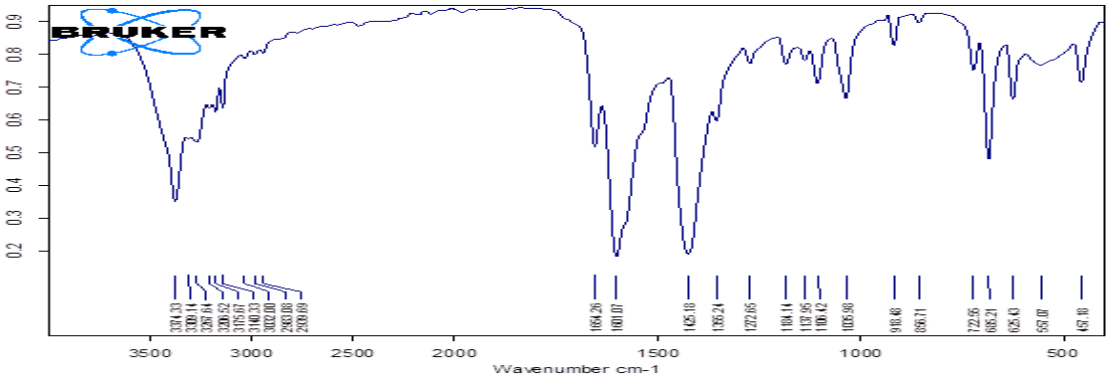
4-rasm. 2-aminobenzoksazol molekulasining effektiv zaryaadlarining taqsimoti, YUBMO va QBMO orbitallarining qoplanishi**.**

2-aminobenzoksazolning ikki oyoqli burchagi planar strukturaga nisbatan yaqin yoki silliq ekanligini namoyon qildi. Nazariy natijalarda farazlarimizdagi chastotalarning mavjud emasligi optimallashtirilgan 2-aminobenzoksazol geometriyasi stabil ekanligini ko‘rsatdi.

Kvant-kimyoviy hisoblashlar shuni ko‘rsatdiki, 2-aminobenzoksazol molekulasidagi azot atomi koordinatsiyada ishtirok etadi, o‘z navbatida bu atomlarning koordinatsiyaga uchrashi komplekslarning IQ-spektrida ν(M-N) va ν(M-O) bog‘larining valent tebranishlari 428-499, 546-554, 618-620 sm-1 chastotalarda namoyon bo‘lishi bilan tasdiqlandi.

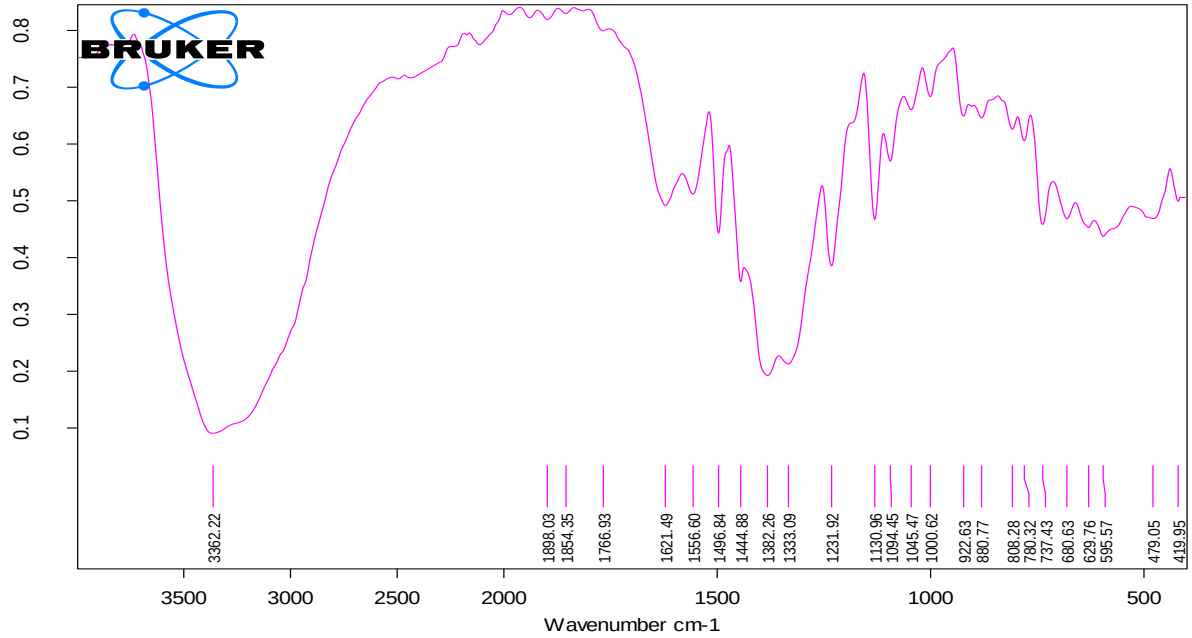


5-rasm. 2-aminobenzoksazolning IQ-spektri

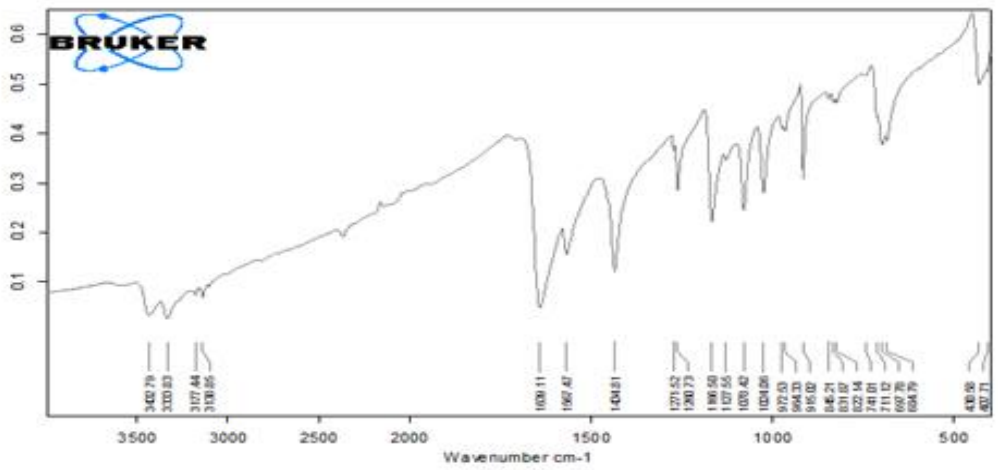


6-rasm. $Cu_2(L)(CH_3COO)_4 \cdot H_2O$ tarkibli kompleksning IQ-spektri

Mis atsetatli kompleks birikmaning IQ spektrida (IQ fure-spektrometr. Bruker Invenio S-2021) interval 4000–400 sm^{-1}. ATR.) 3374-3309 sm^{-1} sohada –N-H bog‘ining valent tebranishlaridan hosil bo‘lgan yutilish maksimumlarini (yoki yutilish chiziqlarini) kuzatish mumkin. 3206-3140 sm^{-1} sohada kompleks birikma tarkibidagi sp^2 gibridlangan =C-H bog‘larining valent tebranishi, 3002-2909 sm^{-1} sohada kompleks birikma tarkibidagi sp^3 gibridlangan -S-H bog‘larining valent tebranishi, 1664-1601 sm^{-1} kompleks birikma tarkibidagi C-N, va C=N bog‘larining valent tebranishi, 1425-1366 sm^{-1} sohada =C-H va -C-H bog‘larining deformatsion tebranishlari, 1184-1006 sm^{-1} sohada -C-O-C- bog‘larining valent tebranishlari, 722-625 sm^{-1} (C_6H_6) –C-H bog‘larining deformatsion tebranishlari, 557-457 sm^{-1} sohada esa Cu-O bog‘ining valent tebranishlari hisobiga yuzaga kelgan yutilish maksimumlarini kuzatishimiz mumkin.



7-rasm. $Co_2(L)(CH_3COO)_4 \cdot H_2O$ tarkibli kompleksning IQ-spektri



Kadmiy atsetat

Kadmiy atsetatli kompleks birikmaning IQ spektrida (IQ fure-spektrometr. Bruker Invenio S-2021) interval 4000–400 sm^{-1}. ATR.) 3420-3300 sm^{-1} sohada –N-H bog‘ining valent tebranishlaridan hosil bo‘lgan yutilish maksimumlarini (yoki yutilish chiziqlarini) kuzatish mumkin. 3217-3046 sm^{-1} sohada kompleks birikma tarkibidagi sp^2 gibridlangan =C-H bog‘larining valent tebranishi, 1691-1592 kompleks birikma tarkibidagi C-N, va C=N bog‘larining valent tebranishi, 1464 sm^{-1} sohada =C-H va -C-H bog‘larining deformatsion tebranishlari, 1271-1064 sm^{-1} sohada -C-O-C- bog‘larining valent tebranishlari, 741-604 sm^{-1} (C_6H_6) –C-H bog‘larining deformatsion tebranishlari, 460 sm^{-1} sohada esa Cd-O bog‘ining valent tebranishlari hisobiga yuzaga kelgan yutilish maksimumlarini kuzatishimiz mumkin.

Xulosa. Sintez qilingan kompleks birikmalarning tarkibi, tuzilishi va xossalari IQ-spektroskopiyasi, SEM-EDX usuli, termik analiz va DQEC kabi fizik-kimyoviy usullar yordamida o‘rganildi. Co(II), Ni(II), Cu(II) va Zn ligand 2-aminobenzoksazol molekulacidagi azot atomi orqali koordinasiyaga uchrashi ko‘rsatildi. Bundan tashqari, termik analiz natijalariga ko‘ra, kompleks birikmalar tarkibida suv molekulalari mavjud ekanligi, shuningdek komplekslarning parchalanishi 200-800^{O}C harorat intervalida sodir bo‘lishi aniqlandi, bu o‘z navbatida yuqoridagi eksperimental tavsifimizni yana bir bor tasdiqladi. Benzoksazolning yangi hosilasi 2-aminobenzoksazol molekulasining reaksion qobiliyatini va kompleks hosil qilish xususiyatlarini o‘rganish maqsadida ayrim 3d-metallarning tuzlari olinib, ular bilan bir necha sintez ishlari olib borildi. Sintez qilingan kompleks birikmalarning tarkibi, tuzilishi va xossalari zamonaviy fizik-kimyoviy tadqiqotlar bilan o‘rganilganda kompleks birikmalar tarkibida metall va atsidoligandlar tabiatining ta’siri kuzatildi.

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