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Synthesis, Characterization and Antimicrobial Evaluation of Mixed Ligand Complexes of Ni (II) and Co (II) 1,2,3-Triazole with Thiocyanate.

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ABSTRACT

The metal complexes of Co^{2+} and Ni^{2+} 1,2,3-triazole mixed ligand have been synthesized. The synthesized complexes in different ratios have been characterized by element chemical analysis, molar conductance and Uv-visible and FTIR spectroscopic studies.IR spectra data suggests the involvement of sulphur and nitrogen in coordination to the central metal ions. On the basis of spectral studies and elemental analysis, a tetrahedral geometry was assigned for the nickel complexes while dimerization was suspected for cobalt(II) complexes.The free ligand and metal complexes were tested in vitro against a number of microorganisms (fungi and bacteria) in order to assess their microbial properties. They are found to be proactive against fungi and bacteria upon the metal complexes, nickel complexes performed better than the cobalt complexes.

INTRODUCTION

In recent years, there has been considerable interest in the synthesis and use of functionalized polymers having chelating abilities due to their practical conveniences, operational flexibility and information of coordination with high metal to polymer bond energies [1,2] .

Sulphur and nitrogen containing 5-membered heterocyclic are known to exhibit useful biological activity [3]. Coumarin derivatives containing sulphur are known to possess antibacterial antifungal activity [4] . Thiazolidinones too exhibit a wide variety of physiological activity [5]. A well known antibiotic, penicillin, has the thiazolidine ring as part of its structure.

Many attempts have been made to synthesis a variety of transitional metal complexes using the 1,2,4-triazole ligands , and their structures and properties were physically and chemically determined 1,2,3-triazoles have attracted great and growing interest in coordination chemistry because of the fact that they can synthesis transition metal coordination polymers with the two bridging close adjacent nitrogen atom (N_1 and N_2 or the 4-positioned one N_4) [6]. This bridge can be of several different geometries, depending on the donor atoms of the ligand and the properties of the metal [7, 8].

Triazole and its derivatives are interesting ligands for their important properties [20]. Because of the position of the donor atoms in the five- membered ring, the triazoles appear to possess the possibility of linking metal ions together. The triazole ligands thereby constitute a bridge between the metal ions.

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Despite this interest in triazole ligands in the development of new magnetic materials, relatively few cobalt(II) complexes were reported [9]. Substituted 1,2,4-triazole-triazoles have been actively studied as bridging ligands between transition meta (II) ions coordinating through their N_1 and N_2 atoms, since their complexes have interesting structures and specific magnetic properties.

Recently, the synthesis and crystal structures of new cobalt(II) and nickel(II) complexes with MBPT (4-p-methylphenyl)-3,5-bis(pyridine-2-yl)-1,2,4-triazole had been reported also triaryltriazole compounds [10] which could be acted as doubly bidentate chelating ligands because of their structural similarity to 4-amino-3,5-bis(pyrindin-2-yl)1,2.4-triazole (ABPT) [11] have been investigated.

This paper has reported the synthesis, characterization and antimicrobial activities of azole-based mixed ligand metal complexes with thiocyanate at different concentrations in order to ascertain their coordination sites and assess their potency

EXPERIMENTAL

Material and Reagents

All the chemicals used were of analytical grade (AR) and were used as purchased. They were Cobalt(II)chloridehaxahydrate and Nickel(II)sulphateheptahydrate (Sigma),potassium thiocyanate(BDH)and 1,2,3-triazole(Aldrich)

Analytical Methods

Sulphate contents of the complexes were analyzed by gravimetric method; metal contents were via complexometric titration. The molar conductance of the solid complexes in DMSO-H_2O mixture was measured by using a modelWPACM35 conductivity meter. The solution of the complexes were run on UV-2500PC UV- visible series(800-200nm).The solid state FTIR spectra of the metal complexes were recorded on a Shimadzu FTIR spectrophotometer using KBr pellets in the range of 400-4000cm^{-1}.

Synthesis of Metal Complexes

The salts of $CoCl_2.6H_20$ and $NiS0_4.7H_20$ were dissolved in a mixture of water and methanol , and added to ligand solution prepared from a mixture of water and methanol in ratio 1:1and 1:2 mole ratio ligand to metal respectively , with stirring on a magnetic stirrer for 3 hrs. The resulting mixture was carefully filtered using sintered glass (porosity4) via the suction pump, washed with suitable solvent, dried under vacuum for 5 days. The thiocyanate metal complexes were also prepared by adding potassium thiocyanate to metals and ligand in ratios 1:1:1 and 1:2:1 respectively following the same procedures.

Biological Activity of the Complexes

Antifungal evaluation of the Complexes

Five organisms screened for this work were *Aspergilius niger, Collentotricum falcatum ,Alternaria solani, Fusarium oxysporium and Rhizoctonia solani.* The 1,2,3-triazole and its metal complexes were directly added to the growth media in varying concentrations (2.5% and 5.0%).5ml of each prepared sample was measured into a conical flask (50ml),25ml of sterile Potato Dextrose Agar was added and mixed properly before pour plating and allowed to set at ambient temperature. A sterile 5mm diameter cork borer was used to inoculate the fungal isolates grown over a period of 72hrs at the centre of the plate. The plates were incubated at $27^0C \pm 2^0C$ for 5-7days.The radial growth of the mycelia of the fungi isolates were measured for every24hrs [12]. The diameter of the zone inhibition produced by the complexes was compared with the benlate.

Antibacterial Screening Test

A-24h old pure broth culture of micro -organisms were used and agar pour plate technique was employed for the tests. The organisms used for the screening are *Staphylococcus aureus ,Escherichia Coli* , *Klebsiella aerogenes. Bacillus subtilis* and *Salmonella typhi*. 2ml of the organism was aseptically injected into the sterilized plates and 20ml sterilized nutrient agar was poured on top of the tested organism aseptically after it has been allowed to cool to 45°C . The medium was swirled gently for even distribution of the inoculums (organism used) in the medium and was allowed to solidify at ambient temperature. Standard cork borer of 5mm diameter was used to make well on the solidified agar into which 0.5 ml of the samples was aseptically introduced, using a pipette. A control

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experiment was set -up with well containing standard antibiotic streptomycin sulphate at 0.2 mg /ml. The plates were incubated at 37°C for 24hrs. The zone of inhibition in radii around the well was measured and recorded appropriately.

RESULTS AND DISCUSSSION

Table 1: % Yield Point and Elemental Analysis

COMPLEXES	RATIO	COLOUR	%YIELD	M.PT.	M	Cl	S	Calculated C	(Found) H
$C0_2L_2Cl(H_20)3\}H_20$	1:1	Green	23.13	230ºC	32.4	9.8	-	13.2	3.9
					(33.6)	(9.8)	-	(14.0)	(4.1)
{CoL(SCN)H20Cl}.$5H_20$	1:1:1	Deep green	61.77	251ºC	17.9	10.8	9.6	10.6	4.4
					(17.9)	(9.9)	(8.8)	(10.0)	(4.03)
$NiLS0_4.2H_20$	1:1	Green	36	250ºC	19.9	-	10.9	8.1	3.4
					(19.7)	-	(10.1)	(8.4)	(3.6)
$NiL_2S0_4.H_20$	1:2	Green	53.3	253ºC	19.9	-	10.9	8.1	4.4
					(18.4)	-	(10.1)	(7.7)	(3.9)
$\{NiL(S04)SCNH_20\}4H_20$	1:1:1	Bluish green	62.6	261ºC	15.85	-	17.3	9.7	3.5
					(14.8)	-	(15.6)	(10.2)	(2.9)
$NiL_2(S0_4)SCN.2H_20$	1:2:1	Bluish green	64.6	263ºC	15.3	-	16.5	15.6	2.6
					(15.2)	-	(15.0)	(16.1)	(3.2)

$L=C_2H_3N_3$

Table 2: Data of Physical Properties of the Metal Complexes:

Complexes	Conductivity (Ohm^{-1} cm mol^{1})	IR (cm^{-1})	Uv-vis.(nm)
$C0_2L_2Cl(H_20)3\}H_20$	3.5	3551(-OH), 1658{N-H} ,840(M-N) ,726(H_20) 439,404 (M-Cl)	270
$\{CoL(SCN)H_20Cl\}5H_20$	5.1	3660(-OH) 2081(-SCN), 841(M-N),731(H_20) 427(M-Cl)	277
$NiLSO_4.2H_20$	4.6	3583(-OH),3394,3149(-NH)1183($S04^{2-}$),801(M-N)	270
$NiL_2SO_4.H_2O$	7.0	3310(-NH), 1103($SO4^{2-}$), 982 (M-N) ,765(H_2O)	277
$NiLSO_4(SCN)H_2O\}4H_2O$	16.0	3336(-OH),3161(-NH),2107(-SCN),1084($SO4^{2-}$) 635 (M-N).	266
$NiL_2SO_4(SCN).2H_2O$	8.0	3242(-OH),3118(-NH),2128(-SCN),1114,1064 ($SO4^{2-}$), 748(-OH), 623(M-N).	270
Ligand($C_2H_3N_3$		3491,3267 (-NH),2809,2661,1727,1596,1461, 1155	597

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Table3: Evaluation of antifungal activities of Triazole Metal Complexesat 2.5% and (5.0% Concentrations)

	Aspergilius niger.	*Collentriculum falctum*	*Alternaria solani*	*Fusanirum oxysporium.*	*Rhizotonia solani*
Exposure Time	24 48 72 96	24, 48, 72,96hrs	24, 48, 72,96hrs	24, 48, 72,96hrs	24, 48, 72,96
{Co_2L_2Cl $(H_2O)_3H_2O$(2.5%)	15 16 18 19	14, 15, 18, 18	18, 23, 24, 25	23, 33, 38, 39	33 36 ,38 38
5.0%	21 29 31, 32	21 23 25 27	20 26 33 33	36 39 46 46	38 ,39, 50 56
{$CoLSO_4H_2O$}$2H_2O$2.5%	32 52 72 73	21, 23, 27, 27	22, 26, 29, 30	25, 40, 49, 50	50, 56, 64, 68
5.0%	37 59 78 78	23 30 37 41	27, 40, 47 51	40 47 53 54	54, 61, 71, 72
{CoL (SCN)Cl H_2O}2.5%	21, 20, 25, 31	21, 23, 27, 27	22, 26, 29, 30	22, 26, 29, 30	40, 48, 54 56
5.0%	28 36 40 41	23 30 37 41	27, 40, 47 51	27, 40, 47 51	,59 63 70 70
CuL_2SO4 $(SCN)_2H_2O$2.5%	40, 49, 70, 74	67, 81, 86, 86	40, 56, 68, 71	74, 86, 89, 91	53, 59, 64, 65
5.0%	49 56 77 79	69 84 88 89	54 60, 70 72	76 89 90 93	59, 63, 70, 74
$NiLSO_4$.$2H_2O$(2.5%)	21, 35, 49, 50	59, 59, 66, 66	23, 36, 48, 50	50, 51, 68, 70	56, 58 64, 65,
5.0%	24, 40, 53, 61	63, 65, 70 71	26, 38, 51, 52	57 71, 76, 76	59 61,69, 70
$NiL_2SO_4.H_2O$ (2.5%)	22, 39, 52, 53	65, 66, 71, 71	37, 52, 56, 56	56, 59, 61, 61	58, 63, 66, 68
5.0%	27, 40, 61 70	69, 71, 74, 74	35, 40, 59 59	63, 74, 76, 77	64, 68, 71, 75
{$NiLSO_4(SCN)H_2O$}$4H_2O$ 2.5%	24, 45, 57 57	66, 68, 79, 79	36, 57, 69, 69	60, 66, 69, 69	58, 66, 69, 69
5.0%	29, 49, 62, 73	69, 73, 75 77	38, 53, 74, 74	65, 78, 80 81	65, 70,74, 76
NiL_2SO4 (SCN).$2H_2O$(2.5%)	28, 48, 59 60	68, 79, 82, 82	37, 58, 70, 73	61, 68, 72, 72	60, 69, 72, 72
5.0%	33, 53, 64 74	70 84, 86,86	40, 59, 76, 77	69, 80, 84 84	66, 71, 76, 77
Ligand2.5%	11	15	12	15	14
1,2,3 -triazole5.0%	15	20	18	20	20
$CoCl_2.6H_2O$(2.5%)	3	8	10	13	6
5.0%	5	10	12	15	12
$NiSO_4.6H_2O$2.5%	6	8	12	13	16
5.0%	8	12	16	18	20
Benlate	NO GROWTH	NO GROWTH	NO GROWTH	NO GROWTH	NO GROWTH

Table4: Antibacterial Activities of Triazole Metal Complexes at different concentrations of 2.5% and (5.0% Concentrations)

Complexes	*Staphylococcus aureus*		*Escherichia coli*		*Klebsiella aerogenes*		*Bacillius subtilis*		*Salmonella typhi*	
{Co_2L_2Cl $(H_2O)_3$}H2O	7	(10)	8	(11)	10	(12)	9	(10.5)	11	(13)
{CoL (SCN)ClH_2O}	9	(11)	9	(12)	10	(13)	12	(13)	12	(13.2)
$NiLSO_4$. $2H_2O$	18	(20)	16	(18)	15	(17)	14	(20)	12	(16)
NiL2SO4H2O	23	(24)	18	(20)	19	(23)	16	(22)	15	(21)
Ni LSO4(SCN)H_2O	21	(25)	21	(23)	20	(25)	16	(25)	20	(22)
NiL_2SO4(SCN).$2H_2O$	23	(27)	21	(24)	23	(26)	21	(28)	(21)	(23)
Ligand	10	(10)	6	(10)	8	(11)	8	(11)	10	(12)
Streptomycin Sulphate	32mm	(38)	26 mm	(35)	27mm	(38)	28mm	(40)	34mm	(41)
$CoCl_2.6H_20$	5	(7)	6	(8)	7.2	(10)	5.8	(7.0)	6.5	(10)
$NiS0_4.6H_20$	11	(13)	10	(13)	10	(13)	10	(14)	12	(16.4)

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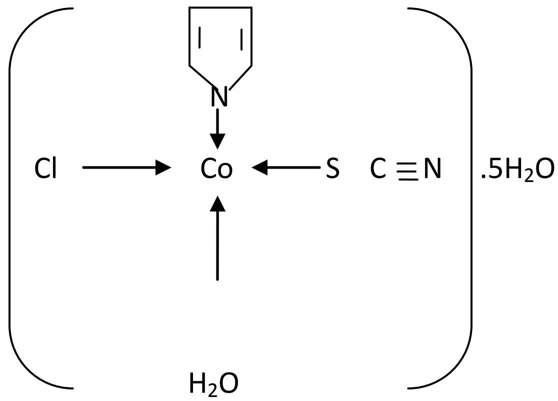
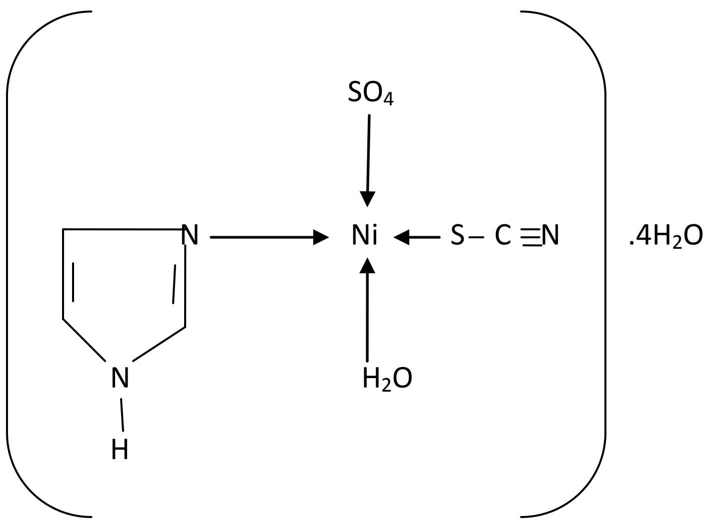


$CoCl_2.6H_2O$ + **L +** SCN ⟶ $CoL(SCN)H_2OCl.5H_2O$ + HCl

(Proposed Structure for Co(II) Mixed ligands)



$[NiL(SO_4)SCNH_2O].4H_2O$ (Proposed Structure)

DISCUSSIONS

The elemental results of the experimental analysis agreed closely with the theoretical values. The solubility tests of the metal complexes revealed that they were not soluble in common organic solvents and water but found to be moderately soluble in a mixture of DMSO-H_2O solution. The melting points of the metal complexes showed sharp melting points difference ±2 ranged between 230-263^{0}C (Table I).The results of the conductivity measurements for the metal complexes revealed that they were non-electrolytes as the recorded values are less than 20.0 ohm^{-1} cm^{3}mol^{-1}.The different colours were achieved for the metal complexes, cobalt(II)complexes showed green and deep green respectively an indication that the ligand 1,2,3-triazole had much effect on the colour formation while the nickel(II)complexes gave green and bluish green which showed that both the ligand and the mixed ligand (potassium thiocyanate) had effect on the colour complexes formation.

The Uv-visble spectrophotometer was used to measure and examine the level of unsaturation and conjugations of the metal complexes. The Uv-visble measurements shared very strong bands or absorption in the region266-277nm in the spectral of the metal complexes which are attributed to n----------> π* transition in the azole ring and CN chromophore for that of the metal complexes an indicative of metal-ligand transfer, this confirms the formation of the bond between the metal ions and the nitrogen atom as 1,2,3-triazole is a tridentate ligand with the ability to coordinate through any of three nitrogen atoms [13,14,15] .FTIR spectra analysis of KBr pellets showed some characteristic results for the metal complexes that were compared with the ligand spectrum. The cobalt(II) complexes showed characteristic peaks at 404-439cm^{-1} which could be attributed to C-Cl and participation of chloride ions in the complexations as confirmed by the gravimetric analysis[16,17].The characteristic peaks around 3267cm^{-1} found in the ligand spectrum but not found in the metal complexes showed that the coordination of the metal to the ligand is through nitrogen atoms ,while strong absorptions around 3551 and 726cm^{-1} were assigned to the -OH group of water coordination molecules which were not appeared in the ligand spectrum.

In Nicke(II) complexes, the characteristics peaks around 983,801,635,623cm^{-1}were attributed to metal coordination to nitrogen atoms of the ligand (1,2,3-triazole) M-N. Furthermore, the strong bands at 1138, 1114, 1103 and 1084cm^{-1} not accurately found in the ligand spectrum were an indication of sulphate ions show the involvement in the complexations as confirmed by the gravimetric analysis .On the other hand, the prominent region at 3267cm-1in the ligand but with shifts in the metal complexes reveal the coordination of metal ions through the nitrogen atom of the ligand. While , a shift in the band 3491cm^{-1} to 3583,3395,3336 and 3242cm^{-1} was attributed to the coordination water from the hydrated metallic salt used for the complexation.

Evaluation of the biocidal activity of the metal complexes were carried out by comparing the results of the metal complexes in percentages with the positive and negative controls; the commercial fungi agent (benlate) and non-treated organisms respectively.

Metal complexeses were screened against the fungi organisms *:Aspergillus niger, conllentrichum falcitum,Alternaria solani, Fusarium oxysporium, and Rhizoctonia solani and bacteria species include Staphylloccus aureus,Escherichia coli,Klebsiella aerogenes,Bacillus substilis and Salmonella typhi.*

The antifungi activity of the metal complexes were screened against the fungi organisms ,the results of the free ligand, the metallic salts and their complexes were compared and found to have potent against the fungi and bacteria .It is known that chelation tends to make ligands act as more powerful and potent fungicidal and bactericidal agents[18].The values indicate that the metal complexes had higher fungicidal and bactericidal activity than the free ligand and metal salts. Such increased activity of the metal complexes can be explained on the basis of the overtone concept of the cell permeability,the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials, due to which liposolubility is an important factor controlling the antimicrobial activity[19,12].However, the metal complexes of the mixed ligand (potassium thiocyanate) appeared more promising than the complexes as has been reported that the metal the biological activity of sulphur containing ligands increases on complexation [21].

It is clear from the antifungi screening data, that the metal complexes are more fungitoxic than the chelating agent.The bacteria screening results reveal that the free ligand 1,2,3-triazole showed minimum activity against bacteria species. The cobalt and nickel complexes showed potent against the microorganisms.In general, the activity of cobalt complexes was the least against the organisms.

CONCLUSION

It can be concluded from the results so far obtained that the ligand 1,2,3-triazole although tridentate in character but coordinates monodentately to the metal ions through the nitrogen atom except cobalt(II) complexes in the ratio 1:1 that gave a dimerized structure.The metal chelate of 1,2,3-triazole possess reasonable antimicrobial potentials.

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