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Synthesis and characterization of novel polymeric biologically active mixed ligand triazole-3-thiones complexes

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ABSTRACT

A series of novel polymeric mixed ligand Co(II), Ni(II), Cu(II) and Cd(II) complexes $[MLL'Cl_2]_mH_2O$ and $[MBHTCl_2 \cdot 2H_2O]_nH_2O$ where M=Co(II), Ni(II), Cu(II), Cd(II); m=0-3; L=4-amino-5-benzyl-4H-1,2,4-triazole-3-thione (ABT), 5-benzyl-4-(benzylidene-amino)-4H-1,2,4-triazole-3-thione (BBT), 5-benzyl-4-[(2-hydroxybenzylidene)-amino]-4H-1,2,4-triazole-3-thione (HBHT) and 5-benzyl-4-[(4-methoxy-benzylidene)-amino]-4H-1,2,4-triazole-3-thione (BMT) as a primary ligands and L'=1,10-phenanthroline mono-hydrate (phen) or α, α' -bipyridyl (bipy) as secondary ligands have been prepared. The analytical data indicated that the interaction between the binary chelates and the secondary ligands proceeds through either substitution or addition reactions. The structures were determined by elemental analysis, molar conductance, magnetic measurements, thermal behaviour, infrared and electronic spectral data. The stoichiometry of synthesized complexes is 1:1:1 or 1:1:2 (metal: primary ligand: secondary ligand). Octahedral structure was proposed for the obtained complexes in which the central metal atom is hexa-coordinated. The low solubility of the complexes in common organic solvents with their magnetic moment values indicated their polymeric nature. The biological activity of the binary chelates enhanced significantly upon their interaction with the secondary ligands.

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KEYWORDS

Synthesis;
Antibacterial activity;
Mixed ligand complexes.

INTRODUCTION

Triazole-3-thiones and their complexes have been reported to be biologically versatile compounds having bactericidal properties. Amine and thione-substituted triazoles have been studied as anti-inflammatory and antimicrobial agents^[1,2]. As such, they are part of the larger family of sulfur and nitrogen containing organic compounds which display a broad range of biological activity, finding applications as antitumor, antibacterial, antifungal and antiviral agents^[3-5]. The chemistry of transition metal complexes with heterocyclic thiones con-

tinues to be of interest, because of their striking structural features as well as their biological importance^[6-8]. However, information on Co(II), Ni(II), Cu(II) and Cd(II) complexes derived from substituted 1,2,4-triazoles is scarce^[9-11].

In this paper we report the synthesis and characterization of novel polymeric mixed ligand triazole-3-thiones complexes with nitrogen donors which consider a continued of our previous work on such family of compounds^[12]. The interaction between the triazole-3-thione binary chelates and the nitrogen donors enhance significantly their biological activities.

RESULTS AND DISCUSSION

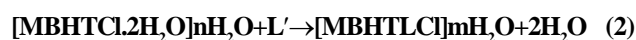
The analytical and physical data of the mixed ligand complexes are given in TABLE 1. The obtained results indicated that the prepared complexes are of good purity and reveal the formation of mixed ligand complexes having 1:1:1 or 1:1:2 (metal ion: primary ligand: secondary ligand) ratio. The obtained data clearly indicate that the secondary ligands phen or bipy used act as neutral bidentate ligands. The suggested structures of the mixed ligand complexes formed indicated that both the two secondary ligands have the same behaviour. In general all the mixed ligand complexes were formed according to addition or substitution reactions:

Addition reaction



where M=Co(II), Ni(II), Cu(II), Cd(II); L=BBT or BMT; L'=phen or bipy; n=0-2; m=0-3.

Substitution reaction



where M=Co(II), Ni(II), Cu(II), Cd(II); L'=phen or bipy; n=0-1; m=0-5.

The methods used for preparation and isolation of these compounds give materials of good purity as supported by their analyses. All the mixed ligand complexes obtained are coloured except the Cd(II) complexes have a white colour expected for d^{10} compounds. The mixed ligand complexes obtained are thermally stable and decompose over 118°C without melting. The solid mixed ligand complexes obtained are stable in air and nonhygroscopic. They are insoluble in common organic solvents but dissolve well in dimethylformamide and dimethylsulphoxide, the observed low solubility of the mixed ligand complexes indicates that they could be polymeric. The complexes 4 and 13 have molar conductance values of 164.10 and 139.6 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively, indicating 1:2 electrolytic nature of these complexes since the reasonable range for 1:2 electrolytes in dimethylformamide solutions is 130-170 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ [18]. The other mixed ligand complexes have molar conductance values of dimethylformamide solutions within the range 19.48-38.53 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ (TABLE 1) indicating the nonelectrolytic nature of these complexes since the reasonable range for 1:1 electrolytes in dimethylformamide solutions is 65-90 Ohm^{-1}

$\text{cm}^2 \text{mol}^{-1}$ [18].

Infrared spectra

Relevant IR bands which provide considerable structural evidence for the mode of attachment of the binary chelate to phen and bipy ligands are reported in TABLE 2 and 3. The IR spectrum of the free phen ligand in the absorption region 1417-1580 cm^{-1} , which is concerned with the ring vibrational modes $\nu(\text{C-C})$ and $\nu(\text{C-N})$, consists of three intense significant bands; the first one close to 1580 cm^{-1} , the second in the neighborhood of 1500 cm^{-1} and the third is located at 1417 cm^{-1} . The first and the second bands usually split into doublet and triplet bands respectively [19]. These bands were shifted to higher frequencies in the mixed ligand complexes. The free phen ligand consistently exhibit two intense bands at 750 and 870 cm^{-1} , the former could be assigned to the out of plane motion of the hydrogen atoms on the heterocyclic ring and the later is due to the hydrogen in the center ring [20,21]. Comparison of these bands with those appeared in the IR spectra of the mixed ligand complexes indicates that these bands are shifted to lower frequencies in the ranges 718-731 and 829-861 cm^{-1} . The fact that all the mixed ligand complexes exhibit intense significant absorption bands at all wave numbers mentioned above confirms the coordination of phen molecule to the binary chelate.

The IR spectrum of the free bipy ligand exhibit a series of significant IR absorption bands appearing in the vibrational regions 3041, 1576, 1552 and 753 cm^{-1} , these bands are apparently the characteristic absorptions of the free bipy ligand [22,23], these bands suffer a positive shift to a higher wavenumber on complexation. This shift attributed to the coordination of the bipy secondary ligand to the binary chelates [24,25]. The $\nu(\text{NH}_2)$ vibrational bands of the binary chelates [12] are shifted to higher frequencies in the IR spectra of the mixed ligand complexes. The band appear in the IR spectra of the mixed ligand complexes within the range 1618-1643 cm^{-1} attributed to $\nu(\text{C=N})$ vibration of the azomethine group. This band shifts to higher frequency in the mixed ligand complexes relative to the binary chelates [12]. The band appearing within the range 3070-3100 cm^{-1} in the IR spectra of the mixed ligand complexes could attributed to the $\nu(\text{NH})$ vibration, this band suffers a shift to higher wave number in the mixed ligand complexes. In most

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TABLE 1 : Analytical and physical data for the mixed ligand complexes

| No. | Complex [Empirical formula] (Formula weight) | Decomp. Temp. (°C) | Color | Yield (%) | Analysis % Found (Calcd.) | | | | Λ_m^* (Ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$) |
|-----|---|-----------------------|--------------------|--------------|---------------------------|----------------|------------------|----------------|---|
| | | | | | C | H | N | S | |
| 1 | [CuBHTphenCl]3H ₂ O (C ₂₈ H ₂₇ ClCuN ₆ O ₄ S) M.Wt.= 642.62 | 220 | Yellowish Green | 51 | 52.52 (52.33) | 4.51 (4.23) | 12.82 (13.08) | 4.73 (4.98) | 26.42 |
| 2 | [CuBMTphenCl ₂]H ₂ O (C ₂₉ H ₂₆ Cl ₂ CuN ₆ O ₂ S) M.Wt.= 657.07 | 228 | Green | 56 | 53.38 (53.01) | 3.75 (3.99) | 12.81 (12.79) | 4.83 (4.88) | 38.53 |
| 3 | [NiBHTphenCl]H ₂ O (C ₂₈ H ₂₃ ClNiN ₆ O ₂ S) M.Wt.= 601.73 | 250 | Greenish Brown | 43 | 56.07 (55.89) | 3.75 (3.85) | 13.93 (13.97) | 5.13 (5.33) | 28.63 |
| 4 | [CoABT(phen) ₂]Cl ₂ .4H ₂ O (C ₃₃ H ₃₄ Cl ₂ CoN ₈ O ₄ S) M.Wt.= 768.58 | 210 | Dark Brown | 50 | 51.31 (51.57) | 4.33 (4.46) | 14.31 (14.58) | 4.25 (4.17) | 164.11 |
| 5 | [CoBHTphenCl]2H ₂ O (C ₂₈ H ₂₅ ClCoN ₆ O ₃ S) M.Wt.= 619.99 | 200 | Dark Brown | 48 | 53.98 (54.24) | 3.96 (4.06) | 13.62 (13.56) | 5.32 (5.17) | 24.95 |
| 6 | [CoBMTphenCl ₂]1.5H ₂ O (C ₂₉ H ₂₇ Cl ₂ CoN ₆ O _{2.5} S) M.Wt.= 661.47 | 218 | Grey | 40 | 52.73 (52.66) | 3.92 (4.11) | 12.90 (12.71) | 4.56 (4.85) | 37.69 |
| 7 | [CdBHTphenCl]0.5H ₂ O (C ₂₈ H ₂₂ CdClN ₆ O _{1.5} S) M.Wt.= 646.44 | >360 | Yellow | 51 | 52.05 (52.02) | 3.36 (3.43) | 12.94 (13.00) | 4.82 (4.96) | 34.89 |
| 8 | [CdBMTphenCl ₂]0.5H ₂ O (C ₂₉ H ₂₅ CdCl ₂ N ₆ O _{1.5} S) M.Wt.= 696.93 | 260 | White | 38 | 49.70 (49.98) | 3.57 (3.62) | 12.18 (12.06) | 5.01 (4.60) | 19.48 |
| 9 | [CuBHTbipyCl]5H ₂ O (C ₂₆ H ₃₁ ClCuN ₆ O ₆ S) M.Wt.= 654.63 | 280 | Pale Green | 49 | 47.60 (47.70) | 4.96 (4.77) | 12.64 (12.84) | 4.99 (4.89) | 27.86 |
| 10 | [CuBMTbipyCl ₂]H ₂ O (C ₂₇ H ₂₆ Cl ₂ CuN ₆ O ₂ S) M.Wt.= 633.05 | 215 | Green | 53 | 51.31 (51.23) | 4.22 (4.14) | 12.93 (13.28) | 4.89 (5.07) | 23.13 |
| 11 | [NiBHTbipyCl]2.5H ₂ O (C ₂₆ H ₂₆ ClNiN ₆ O _{3.5} S) M.Wt.= 604.74 | 220 | Greenish Brown | 55 | 51.89 (51.64) | 4.47 (4.33) | 13.93 (13.89) | 5.28 (5.30) | 23.31 |
| 12 | [NiBMTbipyCl ₂]3H ₂ O (C ₂₇ H ₃₀ Cl ₂ NiN ₆ O ₄ S) M.Wt.= 664.23 | 220 | Yellowish Green | 41 | 48.59 (48.82) | 4.28 (4.55) | 12.31 (12.65) | 4.62 (4.83) | 22.03 |
| 13 | [CoABT(bipy) ₂]Cl ₂ .3H ₂ O (C ₂₉ H ₃₂ Cl ₂ CoN ₈ O ₃ S) M.Wt.= 702.52 | 220 | Dark Brown | 43 | 49.32 (49.58) | 4.33 (4.59) | 16.23 (15.95) | 4.78 (4.56) | 139.62 |
| 14 | [CoBBTbipyCl ₂]2H ₂ O (C ₂₆ H ₂₆ Cl ₂ CoN ₆ O ₂ S) M.Wt.= 616.43 | 200 | Brown | 55 | 50.52 (50.66) | 4.38 (4.25) | 13.72 (13.63) | 5.26 (5.20) | 25.75 |

| No. | Complex [Empirical formula] (Formula weight) | Decomp. Temp. (°C) | Color | Yield (%) | Analysis % Found (Calcd.) | | | | Λ_m^* (Ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$) |
|-----|--|--------------------------|---------------|--------------|---------------------------|----------------|------------------|----------------|---|
| | | | | | C | H | N | S | |
| 15 | [CoBHTbipyCl]2H ₂ O (C ₂₆ H ₂₅ ClCoN ₆ O ₃ S) M.Wt.= 595.97 | 200 | Dark Brown | 49 | 52.49 (52.40) | 4.36 (4.23) | 13.98 (14.10) | 5.23 (5.38) | 27.27 |
| 16 | [CdBBTbipyCl ₂] (C ₂₆ H ₂₂ CdCl ₂ N ₆ S) M.Wt.= 633.88 | 240 | White | 47 | 49.40 (49.26) | 3.32 (3.49) | 13.53 (13.26) | 4.83 (5.06) | 28.26 |
| 17 | [CdBMTbipyCl ₂] (C ₂₇ H ₂₄ CdCl ₂ N ₆ OS) M.Wt.= 663.90 | 270 | White | 53 | 48.77 (48.85) | 3.71 (3.64) | 12.39 (12.66) | 4.79 (4.83) | 33.35 |

*Measured in DMF

TABLE 2 : Some IR frequencies of the free ligands and their mixed ligand complexes (cm⁻¹)

| Compound | $\nu(\text{OH})$ (H ₂ O) | $\nu(\text{NH})/$ $\nu(\text{NH}_2)^*$ | $\nu(\text{C}=\text{N})$ (Azo-methine) | Thioamide bands | | | | phen characteristic bands | | | | |
|---|--|---|---|---|---|---|--------------------------|---------------------------|------|-------|-----|-----|
| | | | | I | II | III | IV | | | | | |
| | | | | $\delta(\text{C}-\text{H})$ + $\delta(\text{N}-\text{H})$ | $\nu(\text{C}=\text{S})+$ $\nu(\text{C}-\text{N})+$ $\delta(\text{C}-\text{H})$ | $\nu(\text{C}-\text{N})$ + $\nu(\text{C}-\text{S})$ | $\nu(\text{C}=\text{S})$ | | | | | |
| phen | 3367 | - | - | - | - | - | - | 1580 | 1500 | 1417* | 870 | 750 |
| [CuBHTphenCl]3H ₂ O | 3411 | 3100 | 1622 | 1560 | 1379 | 970 | 751 | 1600 | 1520 | 1440 | 840 | 722 |
| [CuBMTphenCl ₂]H ₂ O | 3460 | 3100 | 1639 | 1589 | 1355 | 1020 | 776 | 1597 | 1508 | 1418 | 832 | 718 |
| [NiBHTphenCl]H ₂ O | 3360 | 3075 | 1636 | 1565 | 1339 | 1024 | 760 | 1601 | 1512 | 1421 | 844 | 724 |
| [CoABT(phen) ₂]Cl ₂ .4H ₂ O | 3340 | 3258/ 3150* | - | 1578 | 1337 | 1002 | 764 | 1600 | 1512 | 1421 | 844 | 728 |
| [CoBHTphenCl]2H ₂ O | 3408 | 3075 | 1639 | 1577 | 1379 | 1016 | 772 | 1598 | 1516 | 1422 | 837 | 719 |
| [CoBMTphenCl ₂]1.5H ₂ O | 3400 | 3100 | 1640 | 1569 | 1373 | 1024 | 760 | 1600 | 1508 | 1419 | 837 | 731 |
| [CdBHTphenCl]0.5H ₂ O | 3489 | 3100 | 1619 | 1597 | 1384 | 1012 | 785 | 1598 | 1510 | 1421 | 861 | 725 |
| [CdBMTphenCl ₂]0.5H ₂ O | 3420 | 3100 | 1641 | 1583 | 1379 | 1020 | 784 | 1602 | 1512 | 1421 | 829 | 724 |

*: $\nu(\text{NH}_2)$ vibrationsTable 3 : Some IR frequencies of the free α, α' -bipyridyl ligand and its mixed ligand complexes (cm⁻¹)

| Compound | $\nu(\text{OH})$ (H ₂ O) | $\nu(\text{NH})/\nu(\text{NH}_2)^*$ | $\nu(\text{C}=\text{N})$ (Azo-methine) | bipy characteristic bands | | | | Thioamide bands | | | |
|---|--|-------------------------------------|---|---|---|---|--------------------------|-----------------|------|------|-----|
| | | | | | | | | I | II | III | IV |
| | | | | $\delta(\text{C}-\text{H})$ + $\delta(\text{N}-\text{H})$ | $\nu(\text{C}=\text{S})+\nu(\text{C}-\text{N})$ + $\delta(\text{C}-\text{H})$ | $\nu(\text{C}-\text{N})$ + $\nu(\text{C}-\text{S})$ | $\nu(\text{C}=\text{S})$ | | | | |
| Bipy | - | - | - | 3041 | 1576 | 1552 | 753 | - | - | - | - |
| [CuBHTbipyCl]5H ₂ O | 3460 | 3070 | 1618 | 3050 | 1601 | 1568 | 756 | 1568 | 1371 | 992 | 724 |
| [CuBMTbipyCl ₂]H ₂ O | 3460 | 3100 | 1640 | 3080 | 1597 | 1589 | 776 | 1589 | 1355 | 1020 | 726 |
| [NiBHTbipyCl]2.5H ₂ O | 3408 | 3100 | 1639 | 3061 | 1598 | 1565 | 772 | 1565 | 1340 | 1016 | 768 |
| [NiBMTbipyCl ₂]3H ₂ O | 3440 | 3100 | 1643 | 3050 | 1597 | 1569 | 758 | 1569 | 1322 | 992 | 738 |
| [CoABT(bipy) ₂]Cl ₂ .3H ₂ O | 3346 | 3263/3149* | - | 3050 | 1598 | 1561 | 762 | 1561 | 1313 | 1028 | 764 |
| [CoBBTbipyCl ₂]2H ₂ O | 3408 | 3090 | 1640 | 3050 | 1597 | 1564 | 762 | 1564 | 1350 | 1022 | 730 |
| [CoBHTbipyCl]2H ₂ O | 3441 | 3100 | 1636 | 3061 | 1600 | 1568 | 774 | 1568 | 1351 | 1008 | 722 |
| [CdBBTbipyCl ₂] | - | 3090 | 1637 | 3110 | 1602 | 1583 | 784 | 1602 | 1379 | 1020 | 760 |
| [CdBMTbipyCl ₂] | - | 3100 | 1639 | 3051 | 1601 | 1565 | 761 | 1565 | 1358 | 1024 | 728 |

*: $\nu(\text{NH}_2)$ vibrations

TABLE 4 : Electronic spectral data and magnetic moment (μ_{eff}) of the mixed ligand complexes

| Compound | ν_{max} (kK) (ϵ_{max} cm ² mol ⁻¹) | Assignment | μ_{eff} | Compound | ν_{max} (kK) (ϵ_{max} cm ² mol ⁻¹) | Assignment | μ_{eff} |
|---|--|-----------------|--------------------|---|---|-------------|--------------------|
| Phen | 30.96 (1119.40) | N→ π^* | - | [NiBMTbipyCl ₂] ₃ H ₂ O | 16.32 (3.15) | d-d | 3.20 |
| | 35.59 (16791.04) | π → π^* | | | 27.67 (972.97) | LMCT | |
| | 37.58 (24626.87) | π → π^* | | | 32.95 (9000.00) | Intraligand | |
| [CuBHTphenCl] ₃ H ₂ O | 15.87 (30.37) | d-d | - | [CoABT(bipy) ₂] ₂ Cl ₂ .3H ₂ O | 34.06 (9567.57) | Intraligand | 6.07 |
| | 24.92 (4297.52) | LMCT | | | 18.74 (94.47) | d-d | |
| | 29.75 (7851.24) | LMCT | | | 31.91 (12510.64) | Intraligand | |
| | 37.17 (19504.13) | Intraligand | | | 33.30 (13021.28) | Intraligand | |
| [CuBMTphenCl ₂] ₂ H ₂ O | 13.33 (31.60) | d-d | 1.29 | [CoBBTbipyCl ₂] ₂ H ₂ O | 15.15 (39.66) | d-d | 5.27 |
| | 31.73 (7764.71) | Intraligand | | | 31.46 (12517.24) | Intraligand | |
| | 36.61 (10323.53) | Intraligand | | | 33.13 (16310.34) | Intraligand | |
| [NiBHTphenCl] ₂ H ₂ O | 16.42(3.44) | d-d | 3.18 | [CoBHTbipyCl] ₂ H ₂ O | 14.71 (72.65) | d-d | 5.21 |
| | 24.05 (1894.74) | LMCT | | | 23.77 (2474.23) | LMCT | |
| | 34.10 (6947.37) | Intraligand | | | 31.99 (10515.46) | Intraligand | |
| | 37.21 (16736.84) | Intraligand | | | 28.56 (1714.29) | LMCT | |
| [CoABT(phen) ₂] ₂ Cl ₂ .4H ₂ O | 19.36 (79.34) | d-d | 5.26 | [CdBBTbipyCl ₂] | 36.38 (12171.43) | Intraligand | - |
| | 28.16 (3438.02) | LMCT | | | 28.99 (2213.59) | LMCT | |
| | 36.63 (31206.61) | Intraligand | | | 32.55 (3116.50) | Intraligand | |
| [CoBHTphenCl] ₂ H ₂ O | 15.03(41.11) | d-d | 5.15 | [CdBMTbipyCl ₂] | 35.26 (5592.23) | Intraligand | - |
| | 23.55 (2500.00) | LMCT | | | | | |
| | 37.05 (26500.00) | Intraligand | | | | | |
| [CoBMTphenCl ₂] _{1.5} H ₂ O | 16.58 (93.40) | d-d | 5.50 | μ_{eff} : in Bohr magneton : diamagnetic | | | |
| | 34.11 (21411.76) | Intraligand | | of the thioamide group are shifted to higher frequencies | | | |
| | 24.89 (1024.39) | LMCT | | relative to the binary complexes ^[12] . The IR spectra of | | | |
| [CdBHTphenCl] _{0.5} H ₂ O | 24.89 (1024.39) | LMCT | - | the mixed ligand complexes containing hydration and/ | | | |
| | 34.30 (3512.20) | Intraligand | | or coordination water molecules display a broad band | | | |
| | 37.70 (10682.93) | Intraligand | | within the range 3340-3489cm ⁻¹ due to $\nu(\text{OH})$ vibra- | | | |
| [CdBMTphenCl ₂] _{0.5} H ₂ O | 29.75 (2543.05) | LMCT | - | tional modes of the water molecules ^[26] and this was | | | |
| | 34.20 (6198.68) | Intraligand | | confirmed by the results of thermal analysis. | | | |
| | 37.70 (12000.00) | Intraligand | | | | | |
| bipy | 35.48 (15790.39) | π → π^* | - | Electronic spectra and magnetic susceptibility | | | |
| | 15.63 (23.77) | d-d | | measurements | | | |
| | 24.94 (3547.17) | LMCT | | The electronic spectral data of the free phen and | | | |
| [CuBHTbipyCl] ₅ H ₂ O | 29.91 (7396.23) | LMCT | - | bipy ligands and their mixed ligand complexes is de- | | | |
| | 36.23 (14339.62) | Intraligand | | picted in TABLE 4 as well as their corrected magnetic | | | |
| | 13.67 (16.32) | d-d | | moment (μ_{eff}). The importance of the magnetic mea- | | | |
| [CuBMTbipyCl ₂] ₂ H ₂ O | 27.93 (1764.71) | LMCT | 2.02 | surements comes from the fact that it plays an impor- | | | |
| | 37.62 (10058.82) | Intraligand | | tant role in studying the stereochemistry of the com- | | | |
| | 16.95 (11.25) | d-d | | plexes. A medium intensity band with ν_{max} at 30.96kK | | | |
| [NiBHTbipyCl] ₂ .5H ₂ O | 23.80 (1725.00) | LMCT | 2.85 | could be recognized in the electronic spectra of the free | | | |
| | 33.01 (6900.00) | Intraligand | | phen ligand, assigned to n→ π^* transitions, and a high | | | |
| | 34.32 (8550.00) | Intraligand | | intensity bands located in the region 35.59-37.58kK | | | |

of the mixed ligand complexes containing phen and bipy secondary ligands, the IR spectral characteristic bands

of the thioamide group are shifted to higher frequencies relative to the binary complexes^[12]. The IR spectra of the mixed ligand complexes containing hydration and/or coordination water molecules display a broad band within the range 3340-3489cm⁻¹ due to $\nu(\text{OH})$ vibrational modes of the water molecules^[26] and this was confirmed by the results of thermal analysis.

Electronic spectra and magnetic susceptibility measurements

The electronic spectral data of the free phen and bipy ligands and their mixed ligand complexes is depicted in TABLE 4 as well as their corrected magnetic moment (μ_{eff}). The importance of the magnetic measurements comes from the fact that it plays an important role in studying the stereochemistry of the complexes. A medium intensity band with ν_{max} at 30.96kK could be recognized in the electronic spectra of the free phen ligand, assigned to n→ π^* transitions, and a high intensity bands located in the region 35.59-37.58kK attributed to the π → π^* transitions. The electronic spectra of the free bipy ligand displays only one high intensity a significant absorption band in the region 35.48kK attributed to the π → π^* transitions^[19,27-30]. Three sets of bands could be recognized in the electronic spectra

TABLE 5 : Thermal analytical data for the mixed ligand complexes

| Complex | Temp. range°C | Weight loss % | | Loss of moiety | Process | Residue | |
|---|---------------|---------------|-------|---|---------------|-----------------|--------------------------------------|
| | | Calcd. | Found | | | Calcd. (Found)% | Nature |
| [CuBHTphenCl]3H ₂ O | 51-140 | 8.40 | 8.37 | 3H ₂ O | Dehydration | 29.96 (30.04) | CuO-C ₂ HN ₄ S |
| | 233-750 | 61.58 | 61.59 | Cl+phen+C ₇ H ₅ +C ₇ H ₇ | Decomposition | | |
| | 57-115 | 2.74 | 2.63 | H ₂ O | Dehydration | | |
| [CuBMTphenCl ₂]H ₂ O | 185-284 | 24.65 | 24.71 | 2Cl+C ₇ H ₇ | Decomposition | 18.50 (18.61) | CuS-CN |
| | 286-471 | 16.28 | 16.24 | C ₇ H ₇ O | Decomposition | | |
| | 472-750 | 37.77 | 37.81 | Phen+C ₂ H ₂ N ₃ | Decomposition | | |
| [NiBHTphenCl]H ₂ O | 46-132 | 8.88 | 8.84 | H ₂ O+Cl | Deh.+Decom. | 17.73 (17.77) | NiO-S |
| | 146-465 | 27.79 | 27.80 | C ₇ H ₇ +C ₆ H ₄ | Decomposition | | |
| | 466-737 | 45.57 | 45.59 | Phen+C ₃ H ₂ N ₄ | Decomposition | | |
| [CoBHTphenCl]2H ₂ O | 42-103 | 5.81 | 5.71 | 2H ₂ O | Dehydration | 25.63 (25.65) | Co-C ₂ N ₂ S |
| | 142-478 | 32.66 | 32.78 | Cl+C ₇ H ₇ +C ₆ H ₄ | Decomposition | | |
| | 479-750 | 35.84 | 35.86 | Phen+CH ₂ N ₂ | Decomposition | | |
| [CoBMTphenCl ₂]1.5H ₂ O | 43-156 | 4.08 | 4.03 | 1.5H ₂ O | Dehydration | 13.75 (13.65) | CoS |
| | 157-325 | 37.98 | 37.99 | 2Cl+phen | Decomposition | | |
| | 326-470 | 27.51 | 27.62 | 2C ₇ H ₇ | Decomposition | | |
| [CdBHTphenCl]0.5H ₂ O | 471-750 | 16.63 | 16.71 | C ₃ H ₂ N ₄ O | Decomposition | 19.86 (19.86) | CdO |
| | 49-135 | 1.39 | 1.37 | 0.5H ₂ O | Dehydration | | |
| | 200-482 | 33.36 | 33.48 | Cl+phen | Decomposition | | |
| [CdBMTphenCl ₂]0.5H ₂ O | 483-725 | 47.85 | 47.92 | BHT | Decomposition | 28.61 (28.82) | CdS-CHN ₃ |
| | 55-110 | 1.29 | 1.28 | 0.5H ₂ O | Dehydration | | |
| | 218-471 | 40.46 | 40.48 | 2Cl+C ₈ H ₈ O+C ₇ H ₇ | Decomposition | | |
| [CuBHTbipyCl]5H ₂ O | 472-714 | 29.59 | 29.42 | Phen+CN | Decomposition | 26.97 (27.12) | CuS-C ₂ HN ₄ |
| | 58-145 | 19.17 | 19.01 | 5H ₂ O+Cl | Deh.+Decom. | | |
| | 277-750 | 53.80 | 53.87 | Bipy+C ₇ H ₇ +C ₇ H ₅ O | Decomposition | | |
| [CuBMTbipyCl ₂]H ₂ O | 49-117 | 2.84 | 2.74 | H ₂ O | Dehydration | 12.57 (12.57) | CuO |
| | 118-750 | 87.13 | 87.22 | 2Cl+bipy+BMT | Decomposition | | |
| | 40-124 | 7.44 | 7.54 | 2.5H ₂ O | Dehydration | | |
| [NiBHTbipyCl]2.5H ₂ O | 126-175 | 5.87 | 5.72 | Cl | Decomposition | 17.31 (17.41) | NiS-N |
| | 176-466 | 43.19 | 43.24 | Bipy+C ₇ H ₅ O | Decomposition | | |
| | 468-750 | 26.13 | 26.09 | C ₇ H ₇ +C ₂ HN ₃ | Decomposition | | |
| [NiBMTbipyCl ₂]3H ₂ O | 42-113 | 8.13 | 8.11 | 3H ₂ O | Dehydration | 16.06 (16.10) | NiO-S |
| | 161-297 | 22.28 | 22.27 | 2Cl+C ₆ H ₅ | Decomposition | | |
| | 300-479 | 23.51 | 23.43 | Bipy | Decomposition | | |
| [CoABT(bipy) ₂]Cl ₂ .3H ₂ O | 481-748 | 29.96 | 29.99 | C ₁₁ H ₁₁ N ₄ | Decomposition | 9.24 (9.22) | ½ Co ₂ C |
| | 42-117 | 7.69 | 7.58 | 3H ₂ O | Dehydration | | |
| | 170-750 | 83.93 | 83.99 | 2Cl+2bipy+ABT | Decomposition | | |
| [CoBBTbipyCl ₂]2H ₂ O | 43-97 | 5.83 | 5.78 | 2H ₂ O | Dehydration | 18.93 (19.13) | CoS-CN |
| | 200-461 | 49.25 | 49.22 | 2Cl+bipy+C ₆ H ₅ | Decomposition | | |
| | 462-750 | 25.75 | 25.87 | C ₇ H ₇ +C ₂ H ₂ N ₃ | Decomposition | | |
| [CoBHTbipyCl]2H ₂ O | 43-163 | 6.04 | 6.12 | 2H ₂ O | Dehydration | 17.94 (18.04) | CoO-S |
| | 166-381 | 32.16 | 32.02 | Cl+bipy | Decomposition | | |
| | 382-750 | 43.79 | 43.80 | C ₁₆ H ₁₃ N ₄ | Decomposition | | |

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| Complex | Temp. range °C | Weight loss % | | Loss of moiety | Process | Residue | |
|-----------------------------|----------------|---------------|--------|--|---------------|-----------------|------------------------------------|
| | | Calcd. | Calcd. | | | Calcd. (Found)% | Nature |
| [CdBBTbipyCl ₂] | 232-477 | 50.19 | 50.13 | 2Cl+bipy+C ₇ H ₇ | Decomposition | 24.99 (24.99) | CdS-N |
| | 478-750 | 24.77 | 24.89 | C ₇ H ₆ +C ₂ HN ₃ | Decomposition | | |
| [CdBMTbipyCl ₂] | 200-377 | 34.22 | 34.13 | 2Cl+bipy | Decomposition | 33.95 (33.98) | CdS-C ₂ HN ₄ |
| | 378-750 | 31.78 | 31.89 | C ₇ H ₇ +C ₈ H ₈ O | Decomposition | | |

TABLE 6 : Antimicrobial activity of the mixed ligand complexes

| Compound | Bacteria (Inhibition Zone in mm) | |
|---|----------------------------------|-------------------------------|
| | <i>Staphylococcus aureus</i> | <i>Pseudomonas aeruginosa</i> |
| | <i>Vancomycin</i> | - |
| <i>Ceftazimide</i> | 0.6 | - |
| <i>Neomycin</i> | 0.8 | - |
| [CuBHTphenCl]3H ₂ O | 14 | 17 |
| [CuBMTphenCl ₂]H ₂ O | 12 | 15 |
| [NiBHTphenCl]H ₂ O | 10 | 16 |
| [CoABT(phen) ₂]Cl ₂ .4H ₂ O | 9 | 10 |
| [CoBHTphenCl]2H ₂ O | 11 | 13 |
| [CoBMTphenCl ₂]1.5H ₂ O | 6 | 13 |
| [CdBHTphenCl]0.5H ₂ O | 6 | 17 |
| [CdBMTphenCl ₂]0.5H ₂ O | 18 | 15 |
| [CuBHTbipyCl]5H ₂ O | 10 | 15 |
| [CuBMTbipyCl ₂]H ₂ O | 9 | 7 |
| [NiBHTbipyCl]2.5H ₂ O | 8 | 14 |
| [NiBMTbipyCl ₂]3H ₂ O | 10 | 13 |
| [CoABT(bipy) ₂]Cl ₂ .3H ₂ O | 6 | 8 |
| [CoBBTbipyCl ₂]2H ₂ O | 15 | 12 |
| [CoBHTbipyCl]2H ₂ O | 7 | 11 |
| [CdBBTbipyCl ₂] | 4 | 16 |
| [CdBMTbipyCl ₂] | 16 | 13 |

-: No inhibition zone

of the obtained mixed ligand complexes listed in TABLE 4. The first with a ν_{\max} in the range 31.46-37.70kK, could be attributed to intra-ligand charge transfer transitions. The second set includes bands having ν_{\max} in the range 23.55-29.91kK. These bands are assigned to a L→MCT transitions. The third set of bands of Cu(II) complexes was found to have ν_{\max} in the range 13.33-15.87kK. This band is due to a d-d transition which is typical for distorted octahedral Cu(II) complexes^[31]. This band could be assigned to all the three transitions

${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ which are usually found for tetragonal Cu(II) complexes^[31]. The mixed ligand Cu(II) complexes 1 and 9 display a diamagnetic nature (TABLE 4) attributed either to their polymeric nature or super exchange interaction^[32] in complex molecules and/or high polarizability^[33] of the ligands which supplies more electron density to copper ion and consequently the ions interact more strongly. The magnetic moment values for the mixed ligand Cu(II) complexes 2 and 10 at room temperature were found to be 1.29 and 2.02 B.M. respectively. These values are very close to the values expected for spin free octahedral Cu(II) complexes^[32-35], suggesting distorted octahedral geometry for the obtained mixed ligand Cu(II) complexes. Ni(II) mixed ligand complexes were found to give a d-d band with ν_{\max} within the range 16.32-16.95kK. This band could be assigned to the transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, suggesting octahedral geometry^[31]. The room temperature magnetic moments of Ni(II) mixed ligand complexes are within the range 2.85-3.20 B.M. suggesting octahedral geometry^[34-36] for these complexes. The d-d transition bands observed in the obtained Co(II) mixed ligand complexes cover the range 14.71-19.36kK, and could be attributed to the

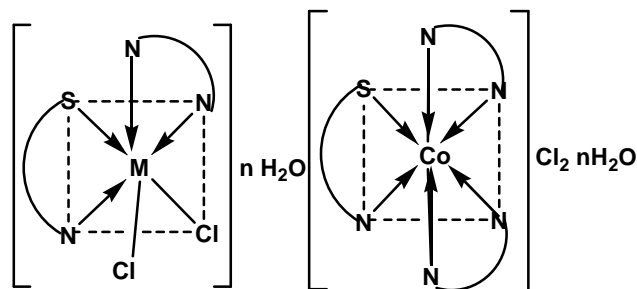
transitions ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(v_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)v_3$, suggesting distorted octahedral environment around Co(II)^[31,34,37]. The room temperature magnetic moment values of the Co(II) mixed ligand complexes are within the range 5.15-6.07 B.M. expected for octahedral Co(II) complexes^[34-36]. The lower magnetic moment values (5.15, 5.21 B.M.) of the complexes 5 and 15 may attributed to the presence of a low symmetry component in the ligands field as well as the covalent nature of the metal-ligand bonds. All the mixed ligand Cd(II) complexes are diamagnetic as ex-

pected for d^{10} system. On the basis of elemental analysis, infrared spectra and thermal analysis, octahedral geometry is suggested for all Cd(II) complexes.

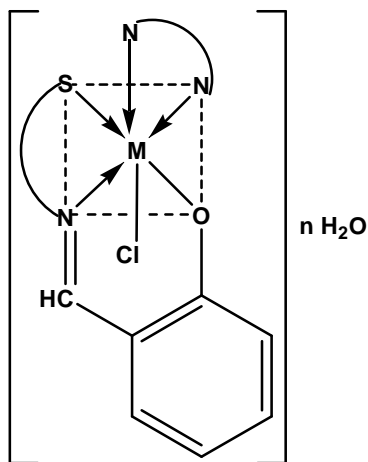
Thermal analysis

The TGA profile of 1,10-phenanthroline mixed ligand complexes indicated that they contains only hydration water molecules (TABLE 5). The thermal behaviour of all complexes display a mass loss on the TGA curves amounting to 1.28-8.37%; (theoretical 1.29-8.40%), corresponding to loss of 0.5-5 hydration water molecules, within a temperature range 42-156 °C. The presence of hydration of water molecules in the prepared α, α' -bipyridyl mixed ligand complexes was verified by TGA (TABLE 5). The thermal behaviour of the bipy mixed ligand complexes (9-15) display as mass loss of 2.74-19.01%; (theoretical 2.84-19.17%), within a temperature range 40-163°C, corresponding to loss of 1-5 hydration water molecules.

Based on the foregoing discussion, the proposed structure of the mixed ligand complexes can be formulated as follows, (Scheme 1):



Where: $\text{N} \cdots \text{S}$ = ABT, BBT, BHT or BMT



where: M = Cu(II), Ni(II), Co(II) or Cd(II); n = 0-5; $\text{N} \cdots \text{N}$ = L = phen or bipy

Scheme 1: Proposed structure for the mixed ligand complexes

Biological testing

A filter paper disc method was employed for the *in vitro* study of antibacterial effects against gram positive bacteria *Staphylococcus aureus* and gram negative bacteria *Pseudomonas aeruginosa*. The following drugs were used as reference materials *Vancomycin*, *Ceftazimide* and *Neomycin*. The inhibitory effects of the mixed ligand complexes against these organisms are given in TABLE 6. The screening results indicate that all mixed ligand complexes exhibited antibacterial activities. Moreover, comparing the obtained data with that of the binary chelates^[12] indicated that the antibacterial activity enhanced on complexation with the nitrogen donor ligands. Also It could be noted that the mixed ligand complexes showed a great inhibitory effects against bacteria compared to those with the well known drugs *Vancomycin*, *Ceftazimide* and *Neomycin*.

EXPERIMENTAL

All chemicals used in the preparative work were of A.R. or equivalent grade, they include the following: carbon disulfide, potassium hydroxide, absolute ethanol, phenylacetic acid, hydrazine, diethyl ether, hydrochloric acid, benzylaldehyde, salicylaldehyde, p-methoxybenzylaldehyde, piperidine, 1,10-phenanthroline mono-hydrate and α, α' -bipyridyl. The metal salts $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ used were of general reagent grade.

Preparation of the ligands ABT, BBT, HBHT, BMT

They were prepared following the literature procedure^[12-15]. ABT was prepared by the interaction of the potassium phenylacetyl dithiocarbamate salt and 95% hydrazine hydrate. BBT, HBHT and BMT were prepared by the interaction of ABT and the corresponding arylaldehyde {benzylaldehyde or salicylaldehyde or p-methoxybenzylaldehyde}.

ABT: m.p. 180°C, yield 63%. The purity of the product ABT was checked by elemental analysis [Calcd.(Found)% for $\text{C}_9\text{H}_{10}\text{N}_4\text{S}$ (ABT) M.Wt.=206.27; C 52.41(52.13); H 4.89(4.71); N 27.16(27.50); S 15.55(15.73).

BBT: m.p. 182°C, yield 65%. The purity of BBT was checked by elemental analysis [Calcd.(Found)%

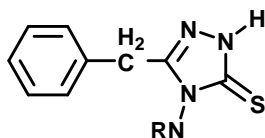
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for $C_{16}H_{14}N_4S$ (BBT) M.Wt.=294.38; C 65.28 (64.98); H 4.79 (4.71); N 19.03 (18.93); S 10.89 (10.71)].

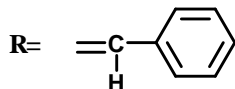
HBHT:m.p. 200°C, yield 61%. The purity of HBHT was checked by elemental analysis [Calcd.(Found)% for $C_{16}H_{14}N_4SO$ (HBHT) M.Wt.=310.38; C 61.92(61.75); H 4.55(4.64); N 18.05(17.99); S 10.33 (9.88)].

BMT:m.p.191-192°C, yield 59%. The purity of BMT was checked by elemental analysis [Calcd.(Found)% for $C_{17}H_{16}N_4SO$ (BMT) M.Wt.=324.408; C 62.94(62.58); H 4.97(4.69); N 17.27(17.05); S 9.88(10.02)].

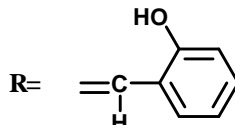
The structures of the primary ligand are given in Scheme 2.



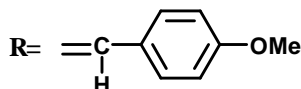
Where, $R = H_2$
4-amino-5-benzyl-4H-1,2,4-triazole-3-thione (ABT)



5-benzyl-4-(benzylideneamino)-4H-1,2,4-triazole-3-thione (BBT)



5-benzyl-4-[(2-hydroxybenzylidene)amino]-4H-1,2,4-triazole-3-thione (HBHT)



5-benzyl-4-[(4-methoxybenzylidene)amino]-4H-1,2,4-triazole-3-thione (BMT)

Scheme 2 : Proposed structure for the primary ligands

Preparation of the binary complexes

They prepared according to the literature procedure^[12]. For this purpose Co(II), Ni(II), Cu(II) and Cd(II) complexes were synthesized by adding hot ethanol solution of the appropriate metal chloride (10^{-3} M) dropwise to a hot ethanol solution of the appropriate ligand (10^{-3} and 2×10^{-3} M) in 1:1 and 1:2 molar ratios and the pH was adjusted to 3.5-4.5 using 5% NaOH solution with constant stirring for 2 hours. Immediate precipitate was obtained in all cases. The products so obtained were filtered through a sintered glass, washed

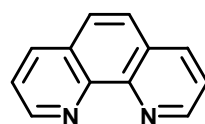
with ethanol, ether and dried in *vacuum* over P_4O_{10} .

Preparation of the mixed ligand complexes

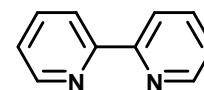
All the mixed ligand complexes were prepared following essentially the same procedure.

A hot methanolic solution (20mL) of the secondary ligand[1,10-phenanthroline monohydrate (phen) or α,α' -bipyridyl (bipy)] (1mmole), added dropwise with constant stirring to a hot refluxed methanolic solution (30mL) of the binary complex (1mmole). The reaction mixture obtained was stirred for an hour and refluxed for 6-8 hours. The obtained solution was evaporated to 50% of its original volume and on cooling the desired compound precipitated, filtered off, washed with methanol. The resulted mixed ligand complex was dried in *vacuum* over P_4O_{10} .

The structures of the secondary ligand are given in Scheme 3.



phenanthroline monohydrate (phen)



α,α' -bipyridyl (bipy)

Scheme 3 : Proposed structure for the secondary ligands

Antimicrobial activity of the complexes

The filter paper disc method^[16,17] was performed using Sabouraud dextrose broth and Mueller Hinton broth. These agar media were inoculated with 0.5 mL of the 24hours liquid cultures containing 10^7 microorganism/mL. Filter paper discs (5 mm diameter) saturated with solutions of the complexes (concentration: 10mg/mL DMF) were placed on the indicated agar media. The incubation time was 24hours at 37°C for bacterial species: gram positive strains *Staphylococcus aureus* and gram-negative strains *Pseudomonas aeruginosa*. Discs with only DMF were used as control. Inhibitory activity was measured (in mm) as the diameter of the observed inhibition zones. The tests were repeated to confirm the findings and the average of the readings was taken into consideration.

Physical measurements

Electronic spectra were run on a Perkin Elmer UV/VIS spectrophotometer Lambda 40 using 1-cm matched silica cells. IR spectra were obtained in KBr discs using 470 Shimadzu infrared spectrophotom-

eter(4000-400cm⁻¹). Conductivity measurements were carried out using CDM216 Meterlab conductivity meter in DMF solutions at 10⁻³ M concentrations at room temperature (~25°C). Magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type MSB-Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants. The calibrant used was Hg[Co(SCN)₄]. Thermogravimetry of the various complexes was carried out using a Shimadzu DTG 60-H thermal analyzer, at a heating rate of 10°C min⁻¹ in a nitrogen atmosphere.

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