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Arylazo derivatives of some fluorinated β -diketones and their metal complexes

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Abstract

Phenylazo and benzothiazolylazo derivatives of trifluoroacetylacetone and hexafluoroacetylacetone have been synthesized and characterized. Analytical and spectral data revealed the existence of phenylazo derivatives in the intramolecularly hydrogen-bonded keto-hydrazone form while the benzothiazolylazo derivatives in the azo-enol form. The monobasic bidentate coordination of the phenylazo derivatives and monobasic tridentate coordination of the benzothiazolylazo derivatives in their Ni(II), Cu(II), Zn(II) and Pd(II) complexes have been established by analytical and spectral data.

Keywords: Fluoro- β -diketones; Benzothiazolylazo- β -diketones; Phenylhydrazones; metal complexes.

1. Introduction

Arylazo derivatives of β -diketones and their metal complexes have gained considerable significance in recent years in view of their medicinal and industrial applications [1]. The substitution of an aryl diazonium group at the active methylenic carbon raises the possibility of azo-hydrazone tautomerism [2, 3]. Phenylazo derivatives of β -diketones exist entirely in the keto-hydrazone form while heteroarylazo derivatives exist predominantly in the azo-enol form [4]. Even though literature is extensive on the synthesis, structural characterization, and applications of metal complexes of arylazo derivatives of β -diketones [4–10], reports are scanty on arylazo derivatives of fluorinated β -diketones. A variety of structures otherwise synthetically inaccessible have been prepared from fluoro- β -diketones [11], while the effect of fluorine substituents upon the chemical reactivity of β -diketones has prompted a number of physico-chemical studies [12]. In addition, utilization of fluoro- β -diketones as chelation extraction agents in a variety of analytical manipulations has been extremely important [13, 14]. In continuation of our studies on arylazo derivatives of β -diketones [4, 6–10], we report here the synthesis and characterization of arylazo derivatives of trifluoroacetylacetone and hexafluoroacetylacetone. Typical metal complexes of these ligand systems were also studied.

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2. Experimental

Carbon, hydrogen, and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents by AAS (Perkin Elmer 2380). The electronic spectra of the compounds were recorded in methanol solutions (10^{-4} mol L⁻¹) on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) were obtained on a 8101 Shimadzu FTIR spectrophotometer, ¹H NMR spectra (CDCl₃ or DMSO-d₆) were measured on a Varian 300 NMR spectrometer, ESR spectra (X-band) were obtained at 77 K using a Varian E 112 ESR spectrometer, and mass spectra were recorded on a Jeol/SX-102 mass spectrometer (FAB using Argon and *meta*-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF at $28 \pm 1^\circ\text{C}$ using a solution of about 10^{-3} mol L⁻¹ concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

2.1. Synthesis of Hptfa and Hphfa

The phenylazo derivatives were synthesized by the coupling of benzene diazonium salt with the β -diketones. Benzene diazonium salt (0.01 mol) was prepared as reported [15]. After destroying the excess nitrous acid with urea, it was added drop by drop to a solution of the β -diketone (0.01 mol in 15 mL ethanol) kept below 0°C with constant stirring. The pH of the solution was maintained around 6, using sodium acetate. The precipitated compound was filtered, washed with water, and recrystallized from ethanol to get chromatographically pure (TLC) material.

2.2. Synthesis of Hbtfa and Hbhfa

An aqueous solution of benzothiazole-2-diazonium ion was prepared by standard method [16]. After destroying the excess nitrous acid with urea, the solution was added drop by drop with stirring to an ice cold ($<5^\circ\text{C}$) solution of the β -diketone (0.01 mol, 20 mL ethanol). Sodium acetate was added to adjust the pH around 6. Stirring was continued for about half an hour and the precipitated compound was filtered, washed with water, and recrystallized twice from hot methanol to get chromatographically (TLC) pure compound.

2.3. Synthesis of metal complexes

A concentrated aqueous solution of metal(II) acetate (0.01 mol, 15 mL) was added to a hot ethanolic solution of the ligand (0.02 mol, 20 mL). The mixture was refluxed on a hot water bath for 10 minutes and then cooled to room temperature. The precipitated complex was filtered, washed with water, recrystallized from hot methanol/chloroform, and dried in vacuum.

3. Results and discussion

The elemental analytical data of the diazo-coupled products (Table 1) indicate that the reaction has occurred in the 1:1 ratio. All the compounds are crystalline in nature and are soluble in common organic solvents. They formed stable complexes with Ni(II), Cu(II), Zn(II) and Pd(II) ions. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance $<10 \Omega^{-1} \text{cm}^{-1}$; 10^{-3} mol L⁻¹ solution) suggest [ML₂] stoichiometry of the complexes except for the Cu(II) complexes of benzothiazolylazo derivatives which have [CuL(OAc)] stoichiometry. The Zn(II) and Pd(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment. The Ni(II) complexes of phenylazo derivatives are diamagnetic and benzothiazolylazo derivatives are paramagnetic.

Table 1

Physical and analytical data of arylazo derivatives and their metal complexes.

| Compound/ Empirical formula | Yield % | M.P. °C | μ_{eff} B.M. | Elemental Analysis: Found (Calculated)% | | | |
|--|---------|---------|----------------------------|--|----------------|------------------|------------------|
| | | | | C | H | N | M |
| Hptfa C ₁₁ H ₉ N ₂ O ₂ F ₃ | 80 | 81 | - | 51.04 (51.16) | 3.48 (3.49) | 10.81 (10.85) | - |
| Hphfa C ₁₁ H ₆ N ₂ O ₂ F ₆ | 75 | 91 | - | 42.33 (42.30) | 1.91 (1.92) | 8.99 (8.97) | - |
| Hbtfa C ₁₂ H ₈ N ₃ O ₂ SF ₃ | 70 | 168 | - | 45.68 (45.71) | 2.52 (2.54) | 13.34 (13.33) | - |
| Hbhfa C ₁₂ H ₅ N ₃ O ₂ SF ₆ | 74 | 170 | - | 39.06 (39.02) | 1.34 (1.36) | 11.29 (11.38) | - |
| [Ni(ptfa) ₂] C ₂₂ H ₁₆ N ₄ O ₄ F ₆ Ni | 70 | 100 | - | 46.16 (46.10) | 2.77 (2.79) | 9.74 (9.78) | 10.18 (10.25) |
| [Ni(phfa) ₂] C ₂₂ H ₁₀ N ₄ O ₄ F ₁₂ Ni | 82 | 136 | - | 38.68 (38.78) | 1.49 (1.47) | 8.30 (8.23) | 8.64 (8.62) |
| [Ni(btfa) ₂] C ₂₄ H ₁₄ N ₆ O ₄ S ₂ F ₆ Ni | 74 | 220 | 2.78 | 41.88 (41.94) | 2.04 (2.04) | 12.22 (12.23) | 8.50 (8.55) |
| [Ni(bhfa) ₂] C ₂₄ H ₈ N ₆ O ₄ S ₂ F ₁₂ Ni | 70 | 170 | 2.66 | 36.18 (36.24) | 1.00 (1.01) | 10.55 (10.57) | 7.44 (7.39) |
| [Cu(ptfa) ₂] C ₂₂ H ₁₆ N ₄ O ₄ F ₆ Cu | 74 | 184 | 1.68 | 45.66 (45.71) | 2.75 (2.77) | 9.66 (9.70) | 10.89 (11.00) |
| [Cu(phfa) ₂] C ₂₂ H ₁₀ N ₄ O ₄ F ₁₂ Cu | 79 | 180 | 1.72 | 38.42 (38.50) | 1.48 (1.46) | 8.24 (8.17) | 9.29 (9.27) |
| [Cu(btfa)(OAc)] C ₁₄ H ₁₀ N ₃ O ₄ SF ₃ Cu | 72 | >300 | 1.70 | 38.56 (38.48) | 2.28 (2.30) | 9.55 (9.62) | 14.61 (14.56) |
| [Cu(bhfa)(OAc)] C ₁₄ H ₇ N ₃ O ₄ SF ₆ Cu | 74 | 220 | 1.71 | 34.14 (34.24) | 1.44 (1.43) | 8.55 (8.56) | 12.88 (12.95) |
| [Zn(ptfa) ₂] C ₂₂ H ₁₆ N ₄ O ₄ F ₆ Zn | 70 | >300 | - | 45.65 (45.57) | 2.77 (2.76) | 9.74 (9.67) | 11.22 (11.28) |
| [Zn(phfa) ₂] C ₂₂ H ₁₀ N ₄ O ₄ F ₁₂ Zn | 68 | 204 | - | 38.33 (38.40) | 1.46 (1.45) | 8.20 (8.15) | 9.42 (9.51) |
| [Zn(btfa) ₂] C ₂₄ H ₁₄ N ₆ O ₄ S ₂ F ₆ Zn | 66 | >300 | - | 41.64 (41.54) | 2.04 (2.02) | 12.14 (12.11) | 9.51 (9.43) |
| [Zn(bhfa) ₂] C ₂₄ H ₈ N ₆ O ₄ S ₂ F ₁₂ Zn | 68 | 208 | - | 36.02 (35.94) | 0.98 (1.00) | 10.56 (10.48) | 8.12 (8.16) |
| [Pd(ptfa) ₂] C ₂₂ H ₁₆ N ₄ O ₄ F ₆ Pd | 67 | 165 | - | 42.44 (42.55) | 2.54 (2.58) | 9.08 (9.03) | 17.18 (17.15) |
| [Pd(phfa) ₂] C ₂₂ H ₁₀ N ₄ O ₄ F ₁₂ Pd | 68 | 220 | - | 36.28 (36.24) | 1.42 (1.37) | 7.58 (7.69) | 14.52 (14.61) |
| [Pd(btfa) ₂] C ₂₄ H ₁₄ N ₆ O ₄ S ₂ F ₆ Pd | 74 | 184 | - | 39.28 (39.22) | 1.93 (1.91) | 11.49 (11.44) | 14.50 (14.49) |
| [Pd(bhfa) ₂] C ₂₄ H ₈ N ₆ O ₄ S ₂ F ₁₂ Pd | 70 | 158 | - | 34.24 (34.19) | 0.98 (0.95) | 9.86 (9.97) | 12.67 (12.63) |

The observed electronic, IR, ¹H NMR and mass spectral data are in conformity with structure **1** (Fig. 1) of phenylazo derivatives (Hptfa and Hphfa) and structure **2** (Fig. 2) of their metal complexes.

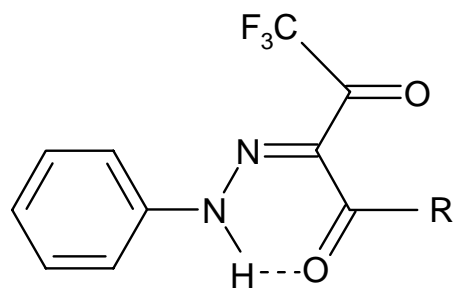


Fig. 1. Structure of Hptfa (R= -CH₃) and Hphfa (R= -CF₃).

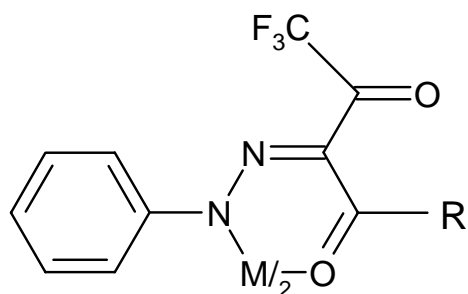


Fig. 2. Structure of the metal complexes of Hptfa and Hphfa (M = Ni(II), Cu(II), Zn(II) and Pd(II)).

The benzothiazolylazo derivatives (Hbtfa and Hbhfa) are in agreement with structure **3** (Fig. 3) and their complexes with structure **4** (Fig. 4). The Cu(II) complexes of Hbtfa and Hbhfa conform to structure **5** (Fig. 5).

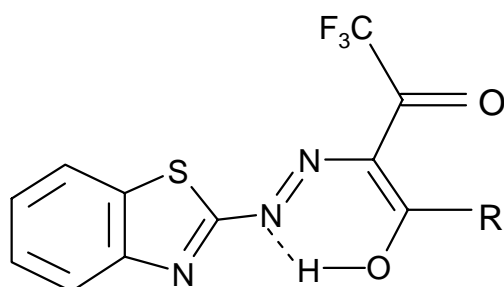


Fig. 3. Structure of Hbtfa (R= -CH₃) and Hbhfa (R= -CF₃).

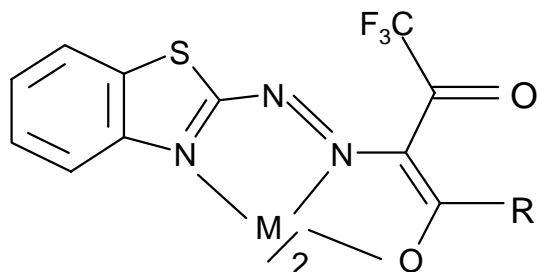


Fig. 4. Structure of the metal complexes of Hbtfa and Hbhfa (M = Ni(II), Zn(II) and Pd(II)).

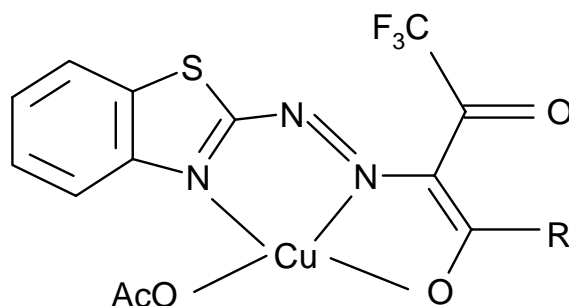


Fig. 5. Structure of the Cu(II) complexes of Hbtfa and Hbhfa.

3.1. Infrared spectra

The IR spectra of Hptfa and Hphfa in the region $1600\text{--}1800\text{ cm}^{-1}$ is characterized by the presence of three strong bands at ~ 1700 , 1640 and 1600 cm^{-1} assignable respectively to the stretching of free trifluoroacetyl carbonyl, intramolecularly hydrogen-bonded carbonyl, and $\text{C}=\text{N}$ stretching vibrations [17,18] of structure **1**. In the spectra of their metal complexes, the band at ~ 1700 and 1600 cm^{-1} of the free ligands remained almost unaffected indicating the non-involvement of trifluoroacetyl carbonyl and $\text{C}=\text{N}$ groups in complexation [19]. However, the band due to the hydrogen-bonded carbonyl at $\sim 1640\text{ cm}^{-1}$ disappeared and instead a new strong band appeared at $\sim 1560\text{ cm}^{-1}$ assignable to the stretching of metal-bonded carbonyl group [6]. A prominent band present in the spectra of the ligands at $\sim 1540\text{ cm}^{-1}$ due to $\nu\text{N-H}$ disappeared in the spectra of all the complexes. This indicates that the metal ion replaced the hydrazone NH proton. Thus the IR spectra of Hptfa and Hphfa strongly support the intramolecularly hydrogen-bonded hydrazone-keto form as in structure **1**. Spectra of the complexes are in agreement with the formation of $\text{C}_2\text{N}_2\text{OM}$ chelate ring as in structure **2**.

The IR spectra of Hbtfa and Hbhfa in the region $1600\text{--}1800\text{ cm}^{-1}$ showed two strong peaks at ~ 1710 and $\sim 1635\text{ cm}^{-1}$ assignable respectively to the stretching of free and enolised carbonyl groups of structure **3**. The two medium intensity bands observed at ~ 1280 and 1430 cm^{-1} are due to C-O-H in plane bending and $\nu\text{N}=\text{N}$ respectively. Thus the IR spectra strongly support the existence of the compounds in the intramolecularly hydrogen bonded azo-enol tautomeric form. In the spectra of the metal complexes, the free trifluoroacetyl carbonyl band of Hbtfa and Hbhfa is only marginally shifted indicating the non-involvement of this carbonyl group in coordination. However the band due to the hydrogen-bonded carbonyl group disappeared and instead a new band appeared at $\sim 1540\text{ cm}^{-1}$ in the spectra of all the complexes supporting the involvement of the enolised carbonyl oxygen in bonding with the metal ion [19]. In the spectra of all the complexes, the band at $\sim 1430\text{ cm}^{-1}$ due to $\nu\text{N}=\text{N}$ and the band due to benzothiazole $\nu\text{C}=\text{N}$ ($1600\text{--}1610\text{ cm}^{-1}$) of the free ligands shifted appreciably to low wave number ($20\text{--}30\text{ cm}^{-1}$) indicating the involvement of these groups in bonding with the metal ion as in structure **4**. In the IR spectra of the Cu(II) complexes of Hbtfa and Hbhfa a comparatively strong band at $\sim 1625\text{ cm}^{-1}$ and a medium intensity band at $\sim 1310\text{ cm}^{-1}$ appeared due to antisymmetric and symmetric stretching of monodentate acetate group [19] as in structure **5**.

The IR spectra of all the four ligands are characterized by the presence of a broad band in the range $2500\text{--}3500\text{ cm}^{-1}$ which clearly indicates the existence of strong intramolecular hydrogen bonding as in structures **1** and **3**. However this broad band disappeared in the spectra of all the complexes and several medium intensity bands due to various $\nu\text{C-H}$ vibrations appeared in the region. These strongly support the replacement of the chelated proton of the ligands by metal ion as in structures **2**, **4**, and **5**. The characteristic out of plane bending and deformation vibrations of CF_3 groups are observed at ~ 1200 and $800\text{--}750\text{ cm}^{-1}$ region [20]. The presence of new medium intensity bands at ~ 425 and 540 cm^{-1} assignable to $\nu\text{M-O}$ and $\nu\text{M-N}$ in the spectra of all the

complexes [19] also support structures **2**, **4** and **5**. Important bands that appeared in the spectra are given in Table 2.

Table 2

Characteristic IR stretching bands (cm^{-1}) of arylazo derivatives and their metal complexes.

| Compound | Free (C=O) | Chelated (C=O) | (C=N) | (C-N) | (N=N) | (M-N) | (M-O) |
|--------------------------|------------------------------|-------------------|--------|--------|--------|-------|-------|
| Hptfa | 1704 s | 1638 s | 1596 s | 1280 s | - | - | - |
| [Ni(ptfa) ₂] | 1702 s | 1556 s | 1598 s | 1268 s | - | 522 m | 416 m |
| [Cu(ptfa) ₂] | 1700 s | 1560 s | 1594 s | 1266 s | - | 520 m | 415 m |
| [Zn(ptfa) ₂] | 1704 s | 1558 s | 1596 s | 1266 s | - | 518 m | 412 m |
| [Pd(ptfa) ₂] | 1700 s | 1562 s | 1592 s | 1264 s | - | 515 m | 408 m |
| Hphfa | 1698 s | 1642 s | 1598 s | 1284 s | - | - | - |
| [Ni(phfa) ₂] | 1696 s | 1558 s | 1596 s | 1266 s | - | 524 m | 418 m |
| [Cu(phfa) ₂] | 1700 s | 1560 s | 1600 s | 1268 s | - | 522 m | 415 m |
| [Zn(phfa) ₂] | 1698 s | 1556 s | 1596 s | 1266 s | - | 518 m | 416 m |
| [Pd(phfa) ₂] | 1702 s | 1564 s | 1594 s | 1266 s | - | 516 m | 410 m |
| Hbtfa | 1705 s | 1638 s | 1608 s | 1268 s | 1432 m | - | - |
| [Ni(btfa) ₂] | 1702 s | 1542 s | 1582 s | 1266 s | 1410 m | 545 m | 418 m |
| [Cu(btfa)(OAc)] | 1706 s, 1626 s, 1312 m | 1540 s | 1580 s | 1264 s | 1413 m | 542 m | 422 m |
| [Zn(btfa) ₂] | 1700 s | 1542 s | 1578 s | 1268 s | 1410 m | 546 m | 420 m |
| [Pd(btfa) ₂] | 1704 s | 1548 s | 1582 s | 1270 s | 1412 m | 540 m | 424 m |
| Hbhfa | 1710 s | 1630 s | 1610 s | 1265 s | 1425 m | - | - |
| [Ni(bhfa) ₂] | 1708 s | 1540 s | 1580 s | 1264 s | 1402 m | 548 m | 428 m |
| [Cu(bhfa)(OAc)] | 1712 s, 1624 s, 1310 m | 1542 s | 1578 s | 1265 s | 1406 m | 540 m | 422 m |
| [Zn(bhfa) ₂] | 1710 s | 1538 s | 1576 s | 1266 s | 1404 m | 546 m | 420 m |
| [Pd(bhfa) ₂] | 1706 s | 1544 s | 1580 s | 1262 s | 1402 m | 542 m | 426 m |

In the case of copper complexes of Hbtfa and Hbhfa two additional bands given under C=O are due to acetate group.

3.2. NMR spectra

In the ¹H NMR spectra of the compounds exhibiting azoenol-ketohydrazone tautomerism, the hydrazone proton usually shows signals at δ 12–15 ppm [3, 21] while the enol proton in the range of δ 9–12 ppm [4, 6, 21]. The ¹H NMR spectra of Hptfa and Hphfa showed one-proton signals at $\sim\delta$ 14.50. The low field resonance signals of Hbtfa and Hbhfa are observed at $\sim\delta$ 11.40 ppm. These confirm the existence of Hptfa and Hphfa in the hydrogen-bonded keto-hydrazone form while Hbtfa and Hbhfa in the azo-enol form. The methyl proton signals of Hptfa and Hbtfa are observed at $\sim\delta$ 2.60 ppm. The aryl proton signals are observed in the range of δ 7.00–7.50 ppm as a complex multiplet. The integrated intensities of all the signals agree well with the structures **1** and **3** of the compounds. In the ¹H NMR spectra of the diamagnetic Zn(II) and Pd(II) complexes, the low field signal due to the chelated hydrogen disappeared indicating its replacement by metal ion during complexation [22] as in structures **2** and **4**. The assignments of various proton signals observed are assembled in Table 3.

Table 3¹H NMR spectral data (δ , ppm) of arylazo derivatives and their Zn(II) and Pd(II) complexes.

| Compound | NH/OH | Phenyl/ Benzothiazolyl | CH ₃ |
|--------------------------|------------|---------------------------|-----------------|
| Hptfa | 14.50 (1H) | 7.12–7.48 (5H) | 2.57(3H) |
| Hphfa | 14.55 (1H) | 7.06–7.40 (5H) | - |
| Hbtfa | 11.48 (1H) | 7.10–7.46 (4H) | 2.53 (3H) |
| Hbhfa | 11.30 (1H) | 7.10–7.50 (4H) | - |
| [Zn(ptfa) ₂] | - | 7.14–7.52 (10H) | 2.62(6H) |
| [Zn(phfa) ₂] | - | 7.08–7.48 (10H) | - |
| [Zn(btfa) ₂] | - | 7.12–7.48 (8H) | 2.56 (6H) |
| [Zn(bhfa) ₂] | - | 7.10–7.52 (8H) | - |
| [Pd(ptfa) ₂] | - | 7.10–7.46 (10H) | 2.59(6H) |
| [Pd(phfa) ₂] | - | 7.04–7.42 (10H) | - |
| [Pd(btfa) ₂] | - | 7.12–7.46 (8H) | 2.61 (6H) |
| [Pd(bhfa) ₂] | - | 7.10–7.52 (8H) | - |

The ¹³C NMR spectrum of Hbhfa clearly indicates its existence in the azo-enol form. That the two carbonyl groups are in different electronic environment is evident from the large separation of the carbonyl carbon signals. The involvement of the enolate oxygen and hetero nitrogen atom in bonding with the metal ion is evident from the positions of the various signals in the ¹³C NMR spectrum of its Zn(II) complex (Table 4). The ¹⁹F NMR spectrum of Hphfa shows two type of fluorine resonance signals at δ 72.5 and 69.5 ppm. The fluorine resonance signal of Hptfa is observed at δ 70 ppm.

Table 4¹³C NMR spectral data (δ , ppm) of Hbhfa and its Zn(II) complex.

| Compound | C=O | Alkyl | C–N | Benzothiazolyl |
|--------------------------|--------------------|------------------|---------|---|
| Hbhfa | 196.036 198.986 | 29.698 31.057 | 164.086 | 121.677, 122.678, 125.465, 126.865, 129.897, 132.453, 150.898 |
| [Zn(bhfa) ₂] | 195.848 196.786 | 29.698 32.867 | 146.086 | 118.386, 118.929, 121.458, 122.063, 122.273, 124.633, 125.780, 127.491, 131.468 |

3.3. Mass spectra

The formulation of the compounds as in structures **1** and **3** is clearly supported from the presence of intense molecular ion peak in the mass spectra. The origin of the peak at m/z 175 in the mass spectra of Hbtfa and Hbhfa can be explained by the formation of the ion radical $BT-N_2CH^+$ (BT = Benzothiazole ring) through the elimination of CH₃CO and CF₃CO from P⁺. If the compounds existed in the hydrazone form, the most facile reaction involves the cleavage of N–N bond and the ion of m/z 175 can not be originated. Presence of peaks due the elimination of BT–N₂ from molecular ion, characteristic of tautomers [23,24], in the spectra of Hbtfa and Hbhfa also support their azo form as in structure **3**. Peaks due to the elimination of C₆H₅N₂ from the molecular ion are not observed in the mass spectra of Hptfa and Hphfa indicating the existence of

the compounds in the hydrazone form as in structure **1**. The origin of the peak at m/z 92 is due to $C_6H_5NH^+$ which is characteristic of the hydrazone form. Fragments due to the elimination of CH_3CO , CF_3CO , C_6H_5 , benzothiazole group, etc. are typical of the spectra of all the compounds. The FAB mass spectra of the Cu(II) complexes of Hptfa and Hphfa showed molecular ion peaks corresponding to $[CuL_2]$ stoichiometry while those of Hbtfa and Hbhfa showed molecular ion peaks corresponding to $[CuL(OAc)]$ stoichiometry. Peaks correspond to $[P - CH_3CO]^+$, $[P - CF_3CO]^+$, $[CH_3CO]^+$, $[CF_3CO]^+$, $[CuL]^+$, L^+ and fragments of L^+ are also present in the spectra. The spectra of the Cu(II) complexes of Hbtfa and Hbhfa also showed peaks due to $[P - CH_3COO]^+$. Important fragments that appeared in the spectra of the ligands and their Cu(II) complexes are given in Table 5.

Table 5

Mass spectral data of arylazo derivatives and their Cu(II) complexes.

| Compound | Mass spectral data (m/z) |
|-------------------|---|
| Hptfa | 258, 215, 166, 161, 118, 97, 92, 77 |
| Hphfa | 312, 220, 215, 118, 97, 92, 77 |
| Hbtfa | 315, 272, 218, 175, 162, 153, 140, 134, 97 |
| Hbhfa | 369, 272, 207, 194, 175, 162, 134, 97 |
| $[Cu(ptfa)_2]$ | 579, 577, 502, 500, 482, 480, 425, 423, 385, 383, 322, 320, 258, 161, 97, 92 |
| $[Cu(phfa)_2]$ | 687, 685, 610, 608, 590, 588, 586, 584, 533, 531, 493, 491, 485, 483, 312, 220, 118, 97 |
| $[Cu(btfa)(OAc)]$ | 438, 436, 341, 339, 379, 377, 315, 304, 302, 282, 280, 276, 274, 218, 175, 140, 134, 97 |
| $[Cu(bhfa)(OAc)]$ | 492, 490, 433, 431, 395, 393, 369, 358, 356, 336, 334, 330, 328, 272, 207, 175, 134, 97 |

3.4. ESR spectra

The ESR spectrum of the Cu(II) complex of Hptfa was recorded at 77 K in DMF solution. The spectrum gave four well-resolved peaks due to the copper hyperfine interaction ($A_{Cu} = 65.8$, $g_{av} = 2.168$) indicating considerable covalent character [25] for the metal-ligand bonds. These values are smaller than that of the non-fluorinated complex due to the greater electronegativity of the CF_3 group.

3.5. Electronic spectra

The UV spectra of the compounds show two broad bands with maxima at ~ 360 and ~ 260 nm due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complexes showed a broad visible band, λ_{max} at $\sim 15,000$ cm^{-1} . This, together with the measured μ_{eff} values (~ 1.70 BM) suggests the square-planar geometry. The observed diamagnetism and broad medium-intensity band at $\sim 17,600$ cm^{-1} in the spectra of the Ni(II) and Pd(II) chelates suggest their square-planar geometry. In conformity, the spectra of the chelates in pyridine solution (10^{-3} M) showed three bands corresponding to configurational change to octahedral due to the association of pyridine [26].

The Ni(II) chelates of Hbtfa and Hbhfa are paramagnetic (μ_{eff} value ~ 2.80 BM) and show three well-separated absorption bands in the spectra at $\lambda_{\text{max}} \sim 8,150$, $\sim 13,350$ and $\sim 24,450$ cm^{-1} corresponding to the transitions; ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively. So the metal ion will be in an octahedral environment.

4. Conclusions

Four new arylazo derivatives were prepared by coupling phenyl diazonium and benzothiazole-2-diazonium ions with trifluoroacetylacetone and hexafluoroacetylacetone. Analytical and spectral data revealed the existence of phenylazo derivatives in the intramolecularly hydrogen-bonded keto-hydrazone form and benzothiazolylazo derivatives in the azo-enol form. The monobasic bidentate coordination of the phenylazo derivatives and monobasic tridentate coordination of the benzothiazolylazo derivatives in their $[\text{ML}_2]$ complexes $[\text{M} = \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)} \text{ and } \text{Pd(II)}]$ have been established by analytical and spectral data. The Cu(II) complexes of benzothiazolylazo derivatives conform to $[\text{CuL}(\text{OAc})]$ stoichiometry. In the metal complexes of the phenylazo derivatives, one of the hydrazone nitrogen and keto oxygen are involved in coordination with the metal ion. In the metal complexes of the benzothiazolylazo derivatives, the donor atoms are one of the azo nitrogen, thiazole nitrogen and one of the carbonyl oxygen.

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