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Synthesis, Spectroscopic Characterization and In-Vitro Antibacterial Activity of Some Cobalt(II) Complexes and Adducts

Omoregie, H.O. and Ibukun, D.T.

Department of Chemistry, Faculty of Science, University of Ibadan, Ibadan, Oyo-State, Nigeria.

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ABSTRACT

Cobalt(II) complexes with 2,4-pentanedione, salicylaldehyde and 4,4,4-trifluoro-1-(2-Naphthyl)-1,3-butanedione(tfnb) as primary ligand, ethylenediamine, 2,2'-bipyridine and 1,10-phenanthroline as secondary ligand have been synthesized and characterized by metal analysis, infrared, electronic spectral studies, conductance, magnetic susceptibility measurements and antimicrobial studies. The conductivity measurement in nitromethane indicates that the complexes and adducts are non-electrolytes while the different shifts of the carbonyl frequencies were revealed by the infrared spectral measurements. The electronic measurements are indicative of a probable six-coordinate octahedral geometry for all the cobalt(II) compounds except $[Co(tfnb)_2]$ with a probable four-coordinate square planar geometry. The ligands and the cobalt(II) compounds were screened for in vitro antimicrobial activity against ten microorganisms. $[Co(tfnb)_2Bipy]$ and $[Co(tfnb)_2en]$ showed more promising antimicrobial than antifungal activity.

Introduction

β-diketones are very important compounds in organic chemistry as they exhibit some interesting biological activities, such as antiulcer, antioxidants, antitumor, antibacterial and antidiabetic activities and are also key intermediate to various heterocyclic compounds [1-5]. They are also being used in UV sunscreen cosmetics that filter certain ultraviolet rays to protect the skin [6] and in thermal transfer printing materials [7]. Salicylaldehyde is also a very important organic compound which is a key precursor to a variety chelating agents. It is used in the formation of Schiff base which have been found to possess various antibacterial properties [8]. In continuation of our studies on *β*-diketones and salicylaldehyde and their derivatives [9-17], we present our report on the synthesis, conductance, magnetic properties, spectral measurements and the antimicrobial study of Cobalt(II) complexes of 4,4,4-trifluoro-1-(2-napthyl) 1,3-butanedione(tfnb) and their 2,2′-bipyridine(bipy), ethylenediamine (en) and 1,10-phenanthroline (phen) adducts. Mixed ligand complex of salicylaldehyde and 2,4-pentanedione and its adducts are also reported.

Preparation of the compounds

Preparation of $[Co(sal)_2(acac)].H_2O$

Salicylaldehyde (0.84 mL, 7.80 mmol) was added to 2,4-pentanedione (0.40 mL, 3.90 mmol) in 2 mL methanol. $CoCl_2.6H_2O$ (0.505 g, 3.90 mmol) in 2 mL distilled water was added in drops into the mixture. The mixture was stirred at room temperature for 1hr till a light-green precipitate was formed. The product formed was then filtered, washed with methanol-water mixture and dried in vacuo.

Preparation of $[Co(sal)(acac)phen].H_2O$

Salicylaldehyde (0.29 mL, 2.74 mmol) was added to 2,4-pentanedione (0.28 mL, 2.74 mmol) in 2 mL methanol. $CoCl_2.6H_2O$ (0.6519 g, 2.74 mmol) in 2 mL distilled water was added in drops into the mixture. The mixture was stirred at room temperature for few minutes, then (0.49 g, 2.74 mmol) of 1,10-phenanthroline was added. The reaction mixture was stirred for 1hr. The dark yellow precipitates formed were filtered, washed with methanol-water mixture and dried in vacuo.

Other adducts of cobalt(II) complex were synthesized following similar procedure

Preparation of $[Co(tfnb)_2]$

A solution of $CoCl_2{\cdot}6H_2O$ (0.23 g, 0.94 mmol) in water (1.2 mL) was added to 4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione (0.50 g, 1.88 mmol) in methanol (5 mL). The mixture was stirred for one hour and the orange solid product was collected by filtration, washed with water and methanol, and dried *in vacuo*.

Preparation of $[Co(tfnb)_2phen]$

A solution of $CoCl_2{\cdot}6H_2O$ (0.23 g, 0.94 mmol) in water (1.2 mL) was added to a mixture of 4,4,4-trifluoro-1-(2-napthyl) 1,3-butanedione (0.50 g, 1.88 mmol) and 1,10-Phenanthroline(0.19 g, 0.94 mmol) in methanol (5 mL). The mixture was stirred for one hour and the pink solid product was collected by filtration, washed with water and methanol, and dried in vacuo. Similar procedure was used for the preparation of the 2,2′-bipyridine and ethylenediamine adducts of the complex.

Antimicrobial screening

The antimicrobial screening was carried out in the Pharmaceutical Microbiology, Faculty of Pharmacy University of Ibadan. Ten microorganisms were used in the screening using a disc diffusion test. This test was performed to screen and determine the complex potential according to their inhibition zone diameter. A mass of the culture medium (Nutrient agar and Sabouraud Dextrose agar) was weighed and dissolved in distilled water. The mixing was heated to homogenize and sterilized in an autoclaved for 15 minutes which was then pour into a Petri dish and left to solidify.

Tele:

E-mail address: tolaomoregie@gmail.com

The compounds were weighed and dissolved in 2mL of methanol making a concentration of 50mg/mL, from which serial dilution of about four more concentration was prepared.

A colony from a 24 hours fresh culture of the various organisms was dissolved in 5mL of sterile distilled water which was spread on the prepared culture agar. Sizeable hole was bore on the culture plate and the dissolved different concentration of the complex was added into each hole. The Petri dishes were then incubated for 24 hours for the bacteria and 48 hours for fungi before the inhibition zone diameters was measured. The results are presented in Table 5.

Physical measurements

The percentage metal in the cobalt(II) compounds were determined by titrimetric method with EDTA. The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using Digital conductivity meter (Labtech). The magnetic susceptibilities of the compounds at room temperature were measured using Sherwood magnetic susceptibility balance. The infrared spectra were measured using nujol on Perkin Elmer Spectrophotometer 11 FT-IR. The solid reflectance and the solution spectra of the compounds were recorded on a Perkin Elmer Lambda double beam UV/VIS spectrophotometer.

Results and discussion

Table 1 shows the analytical data, colour, %yield and room temperature magnetic moments (μ_{eff}) of the prepared cobalt(II) complexes and adducts. The % metal analyses were in good agreement with those calculated for the proposed formula. The cobalt(II) compounds were generally pink in colour except [Co(tfnb)$_2$] which had an orange colour.

Infrared Spectra

Selected infrared bands of the ligands and cobalt(II) complexes and adducts are recorded in Table 2. The assignments of the bands were made by comparing the ligands with those of the literature [10-17]. The infrared spectra of β-diketones usually show coupling of different vibrational modes due to overlap of absorption frequencies [18]. In the ligands studied, the absorptions in the 1728-1516 cm^{-1} region have been assigned to ν_{as}(C=O)+ν_{as}(C=C) vibrations [18,19,20]. In the cobalt complexes and adducts bands in the 1659-1532 cm^{-1} have been assigned as ν_{as}(C=O)+ν_{as}(C=C).

These bands were shifted to 1653-1537 cm^{-1} upon coordination, which confirms the involvement of the C=O in coordination to cobalt(II). Likewise, upon adduct formation, a further shift of this coupled band was observed at 1659-1515 cm^{-1}. This shift could be attributed to a weakening of the M–N bonds on adduct formation. The bands at 866-726 cm^{-1} in the adducts are attributed to CH deformation bands of 2,2′-bipyridine and 1,10-phenanthroline.

Magnetic Moment and Electronic Spectra

The magnetic moments of the cobalt complexes and adducts are recorded in table 1. The room temperature magnetic moment of four coordinate square planar cobalt(II) complexes are expected in the range 2.1-2.8 B.M. [21]. An observed magnetic moment of 2.45 B.M. for [Co(tfnb)$_2$] is suggestive of square planar geometry [22].

The six-coordinate complexes of cobalt(II) are usually high-spin with magnetic moments in the range 4.54-5.26 B.M which shows that there is a large orbital contribution to the magnetic moment since the spin only moment is 3.88 B.M. Stoufer et al. have reported octahedral cobalt(II) complexes with magnetic moments 3.16 and 3.72 B.M. [23] The observed moments for the prepared compounds are in the range 4.54-5.26 B.M which is suggestive of high spin octahedral cobalt(II) compounds [21] except [Co(tfnb)$_2$phen] with a moment of 3.71 B.M. [23].

The electronic spectra of the ligand, synthesized cobalt complexes and adducts in chloroform are presented in table 3 while the electronic solid reflectance spectra are presented in table 4.

In the tfnb ligand, π_3-π^*_4 was observed at 34,364 cm^{-1} region. Bathochromic shift of this band occurred on formation of [Co(tfnb)$_2$] complex. The π_3-π^*_4 band was shifted from 33,898 cm^{-1} to 33,784 cm^{-1}in all the adducts. [Co(tfnb)$_2$] gave absorptions at 14,925 cm^{-1} and 20,000 cm^{-1} while its adducts have bands in the range18,248-18,416 cm^{-1} in chloroform. The bands observed in [Co(tfnb)$_2$] indicate a four coordinate square planar geometry and are assigned as $^2B_{1g}\leftarrow{}^2A_g$ and metal to ligand charge transfer respectively [21] while the bands observed in the adducts are typical of six-coordinate octahedral complexes and are assigned as $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ transition [24]. The solid reflectance of [Co(sal)$_2$(acac)].

Table 1. Analytical and physical data of cobalt(II) complexes and adducts.

Compounds	Mol. wt. (g mol^{-1})	Colour	M.pt(^{o}C)	%Metal Exp (Cal)	Yield%	μ_{eff} (BM)
[Co(sal)$_2$(acac)].H$_2$O	418.01	Yellow	>300	14.61 (14.09)	32	5.15
[Co(sal)(acac)phen].H$_2$O	479.39	Yellow	227-229	12.20 (12.70)	30	4.70
[Co(sal)(acac)bipy].H$_2$O	455.36	Yellow	>300	13.47 (13.78)	14	5.26
[Co(sal)(acac)en].H$_2$O	395.28	Bronwish Yellow	220-223	16.40 (17.12)	32	4.60
[Co(tfnb)$_2$]	589.37	Orange	170-172	10.38(10.0)	55	2.45
[Co(tfnb)$_2$phen]	787.59	Pink	217-220	7.46(7.74)	53	3.71
[Co(tfnb)$_2$bipy]	745.56	Pink	231-233	7.89(7.97)	41	4.63
[Co(tfnb)$_2$en]	649.47	Pink	252-254	9.10 (9.30)	70	4.54

Table 2. Relevant infrared bands (cm^{-1}) of cobalt(II) complexes and their adducts.

Compounds	C=O, C=C	νs(C-H) phen/bipy
acacH	1728w,1709s, 1620vs	
sal	1666s, 1647w, 1621s, 1580vs	
[Co(sal)2(acac)].H2O	1653vs, 1625w,1531s	
[Co(sal)(acac)en].H2O	1653vs,1645w,1600vs,1521vs	
[Co(sal)(acac)phen].H2O	1632vs, 1588s, 1515vs	845vs,727vs
[Co(sal)(acac)bipy].H2O	1658vs,1626w,1531vs,1519w	777vs
tfnb	1603s,1516w	
[Co(tfnb)2]	1605s, 1537w	
[Co(tfnb)2Phen]	1659w,1612s, 1527w	866w, 726w
[Co(tfnb)2Bipy]	1604vs, 1574w,1527s	760s
[Co(tfnb)2en]	1607vs, 1579w,1532s	

Table 3. Relevant electronic solution spectra of cobalt(II) of 4,4,4-trifluoro-1-(2-napthyl)1,3-butanedione and their 2,2′-bipyridine, ethylenediamine and 1,10-phenanthroline.

Compounds	d-d	C.T./ π-π* transitions	Tentative Geometry
tfnb		28,986, 34,364, 37,453, 39,370, 47,847	
$[Co(tfnb)_2]$	14,925, 20,000	29,240, 33,898	Square planar
$[Co(tfnb)_2Phen]$	18,416	28,986, 33,784	Octahedral
$[Co(tfnb)_2Bipy]$	18,248	28,653, 30,030, 33,784	Octahedral
$[Co(tfnb)_2en]$	18,248	30,030, 33,784	Octahedral

Table 4. Relevant electronic solid reflectance spectra of cobalt(II) complex of salicyaldehyde, 2,4-pentanedione and its 2,2′-bipyridine, ethylenediamine and 1,10- phenanthroline Adducts.

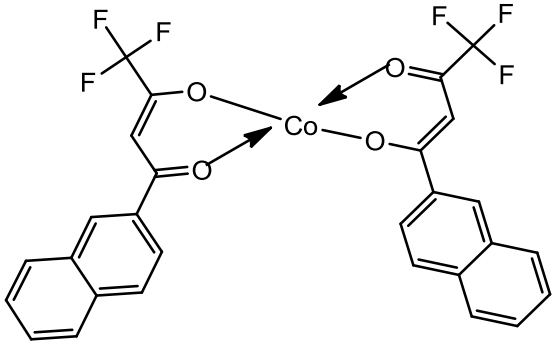
Compounds	d-d	π-π* transitions	Tentative Geometry
[Co(sal)2(acac)]. H2O	15,625	33,956, 39,840	Octahedral
[Co(sal)(acac)en].H2O	14,728	33,898, 40,000	Octahedral
[Co(sal)(acac)phen]. H2O	13,596	33,840, 40,080	Octahedral
[Co(sal)(acac)bipy]. H2O	15,625	33,898, 40,000	Octahedral

H_2O and adducts showed absorption in the range 13,596-15,625 cm^{-1} typical of octahedral complexes and are assigned as $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ [24]. The coordination numbers of the compounds also support the geometry proposed.

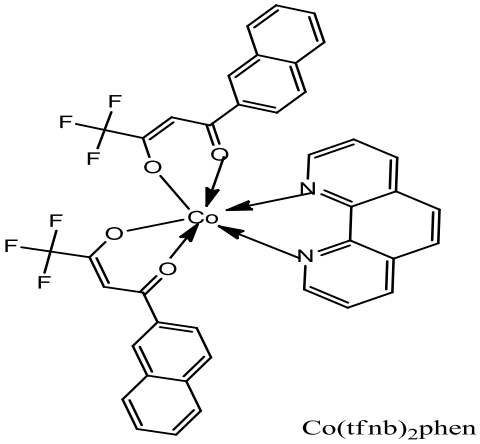
Antimicrobial susceptibility testing

The results for the antimicrobial susceptibility testing are recorded in table 5. The tfnb ligand is active against all the bacteria tested but moderately active against the fungi except *Candida albicans* with pronounced activity. Notably, the ligand (tfnb), $[Co(tfnb)_2Bipy]$ and $[Co(tfnb)_2en]$ were pronounced in their inhibitory activity against the bacteria than $[Co(tfnb)_2]$ and $[Co(tfnb)_2phen]$ and can be described as being more antibacterial than antifungal. The $[Co(sal)_2(acac)].H_2O$ and the adducts were tested against four bacteria and one fungi as recorded in table 5. $[Co(sal)(acac)en].H_2O$ had a very pronounced activity compared to the others in this series.

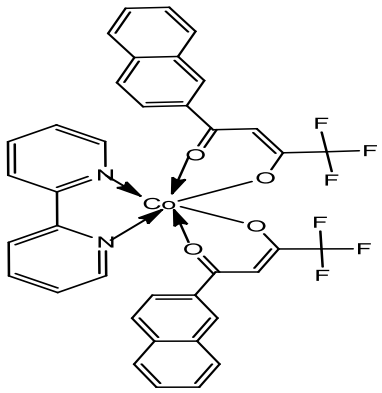
Proposed structures



$Co(tfnb)_2$



$Co(tfnb)_2phen$

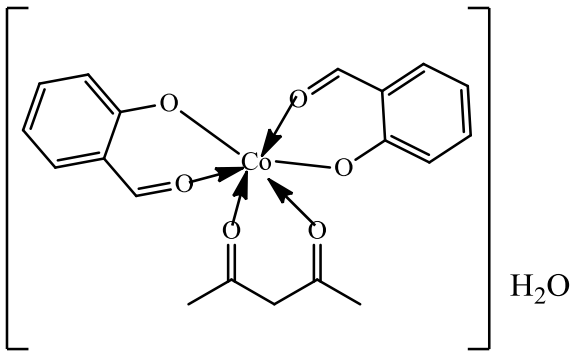


$Co(tfnb)_2bipy$

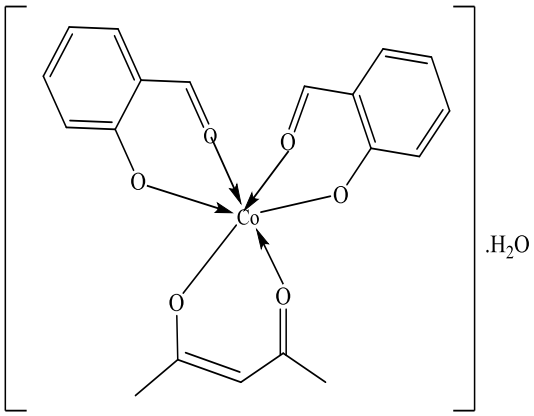
Table 5. Antimicrobial activity of cobalt(II) complexes and adducts.

Compounds	*S. aur*	*E. coli*	*B. sub*	*P. aer*	*S. typhi*	*K. pne*	*Ca*	*An*	*Pen*	*Rs*
tfnb	S	S	S	S	S	S	S	MS	MS	MS
$[Co(tfnb)_2]$	MS	MS	MS	MS	R	R	MS	R	R	R
$[Co(tfnb)_2Phen]$	MS	MS	MS	MS	MS	MS	MS	R	R	MS
$[Co(tfnb)_2Bipy]$	S	S	S	S	S	S	MS	MS	R	R
$[Co(tfnb)_2en]$	S	S	S	S	S	S	S	MS	MS	MS
$[Co(sal)_2(acac)].H_2O$	S	MS	S	MS	ND	ND	S	ND	ND	ND
$[Co(sal)(acac)phen].H_2O$	S	S	S	MS	ND	ND	MS	ND	ND	ND
$[Co(sal)(acac)bipy].H_2O$	S	MS	MS	M	ND	ND	S	ND	ND	ND
$[Co(sal)(acac)en].H_2O$	VS	VS	VS	VS	ND	ND	VS	ND	ND	ND
Gentamycin/ *Tioconazole	MS	ND	MS	MS	ND	MS	MS	MS	ND	ND
Methanol	No activities									

S. aur = Staphylococcus aureus ; B. sub = Bacillius subtilis; K. pne = Klebsiella pneumonia;
E. coli = Escherichia coli; S.typi=Salmonella typhi; P. aer = Pseudomonas aeruginosa;
Ca = Candida albicans ;An = Aspergillus niger ; Pen = Penicillium notatum
Rs=Rhizopus stolonifer; R= organism resistant to the extract; MS=organism moderately sensitive to extract; S=organism adequately sensitive to extract; ND=not done



$[Co(sal)_2acac].H_2O$



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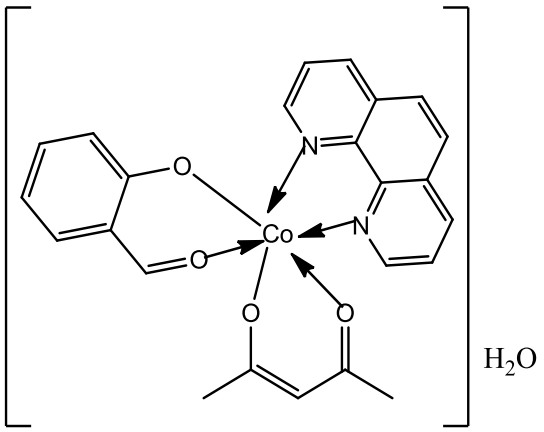
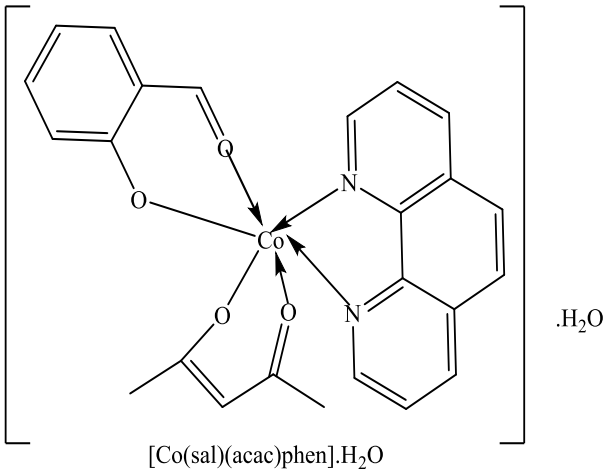
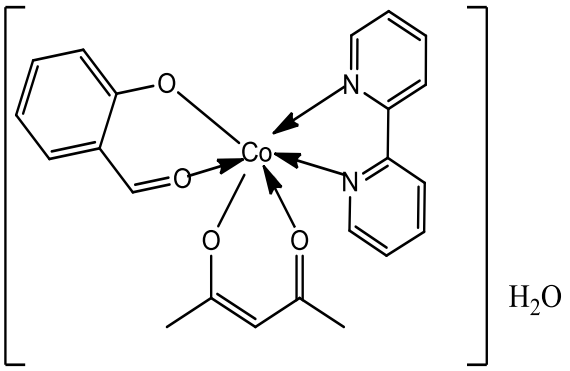


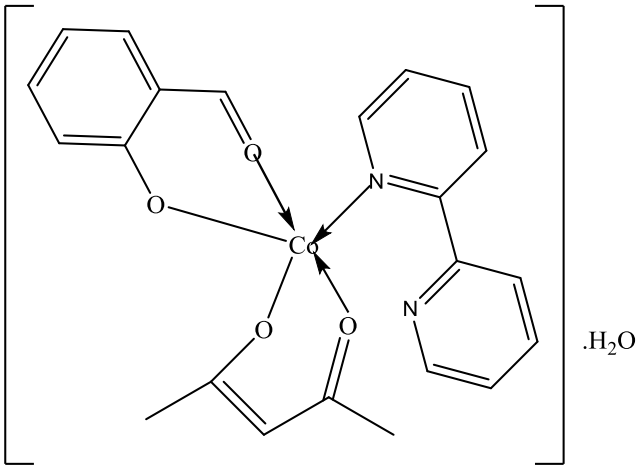
$[Co(sal)(acac)phen].H_2O$



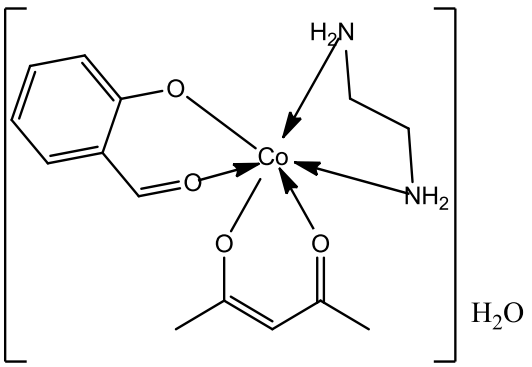
$[Co(sal)(acac)phen].H_2O$



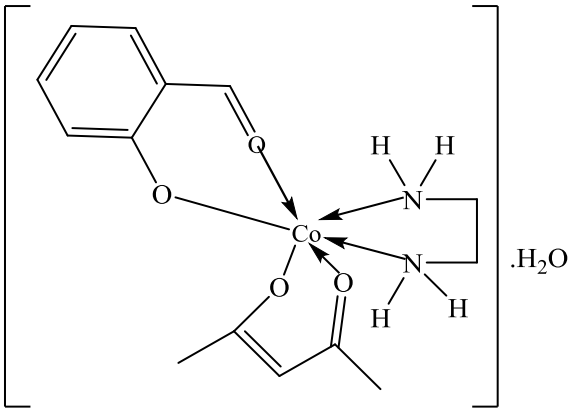
$[Co(sal)(acac)bipy].H_2O$



$[Co(sal)(acac)bipy].H_2O$



$[Co(sal)(acac)en].H_2O$



$[Co(sal)(acac)en].H_2O$

Conclusion

The salicyaldehyde coordinates to the cobalt(II) ion in a bidentate manner through the oxygen of the OH group and CO while the β-diketone ligands coordinate through two oxygen atoms of the acac/tfnb. On the basis of the magnetic and spectral data of the compounds, a probable six-coordinate octahedral geometry is proposed for all the cobalt(II) compounds except $[Co(tfnb)_2]$ with a probable four-coordinate square planar geometry. $[Co(sal)(acac)en].H_2O$ had a very pronounced activity compared to the others in this series.

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