

Synthesis, Spectral Characterization and Biological Activity of Metal(II) Complexes of 2,4,5-Trimethoxybenzaldehyde-S-Benzylthiocarbazonate

DEEPAK KUMAR¹, ARUN KUMAR SINGH¹, AJAY KUMAR¹, DAYANAND PRASAD¹, VIJAY KUMAR² and SHIVADHAR SHARMA^{1,*}

¹University Department of Chemistry, Magadh University, Bodhgaya-824234, India

²P.G. Department of Chemistry, Raj Narain College, Hazipur-844101, India

*Corresponding author: E-mail: sharma.shivadhar@gmail.com

Received: 1 October 2019;

Accepted: 30 October 2019;

Published online: 18 November 2019;

AJC-19700

2,4,5-Trimethoxybenzaldehyde was condensed with S-benzylthiocarbazonate to give Schiff base 2,4,5-trimethoxy benzaldehyde-S-benzylthiocarbazonate (BBTC), which was used for complexation with Mn(II), Fe(II) and Co(II) metal ions. The complexes were formulated as $M(BBTC)_2X_2$ where X is Cl^- , NO_3^- and CH_3COO^- . The FTIR spectra of the metal complexes in comparison to that of free ligand suggested the coordination through azomethine nitrogen and thion sulphur forming six membered chelating with metal ion. The magnetic susceptibility and electronic spectral bands revealed octahedral symmetry (O_h) around Mn(II) but tetragonally distorted octahedral symmetry (D_{4h}) of Fe(II) and Co(II) complexes. The positive value of D_t for Fe(II) (68.42-135.2 cm^{-1}) and Co(II) (263-280 cm^{-1}) clearly indicated elongation along z-axis in these complexes which was also supported by the less value of $Dq_{(z)}$ than $Dq_{(xy)}$ for the metal complexes. The ligand as well as its metal complexes have been found active against the bacteria *Escherichia coli* and *Staphylococcus aureus*, and antibacterial activity of the free ligand has been observed to have enhanced in metal complexes.

Keywords: Metal(II) complexes, 2,4,5-Trimethoxybenzaldehyde, S-benzylthiocarbazonate, Biological activity.

INTRODUCTION

The synthesis, spectral investigation and biological activities of carbazones, thiocarbazonates and their metal complexes have extensively been studied because of their wide variation in modes of coordination, stereochemistry and beneficial pharmacological activities [1-3]. Thiocarbazonates have also been reported as interesting chromogenic reagent that gives intense coloured complexes, shows more bathochromic shift, more sensitivity and more selectivity. Due to the reason this field has attracted the considerable attention of inorganic chemists [4-9]. Schiff's bases of carbazones and thiocarbazonates are considered as good chelating agents. As chelation causes drastic changes in the biological properties of the ligands as well as the metal moiety, such metal complexes have been found potentially, antibacterial, antifungal, anticancer, etc. [10-16].

Due to pharmaceutical properties of carbazones and thiosemicarbazones which are frequently higher for metal complexes than free ligands, they have extensively been studied in recent years [17-20]. However, Schiff base derived from

2,4,5-trimethoxybenzaldehyde and S-benzylthiocarbazonate has scarcely been focused. Particularly, S-benzylthiocarbazonate derived Schiff bases have been found to possess anticancer and antimicrobial activities [21-23]. At the same time, trimethoxybenzaldehyde has been found pharmacologically active as it has been used in the synthesis of drugs like trimethoprim, cinnarizine, etc. [24]. Moreover, metal complexes of various ligands have been reported with distorted octahedral geometry or simply octahedral geometry [25-28]. Their reports however, lack the derivation of even crystal field parameters, let alone the derivation of tetragonal distortion parameters, D_t and D_s . Motivated by these facts and in continuation of our work [29-32] dealing with tetragonally compressed octahedral complexes, we report herein, tetragonally elongated octahedral complexes with positive value D_t and D_s parameters. This study also deals with derivation of Racah parameters B and C for Mn(II) complexes with screening of 2,4,5-trimethoxybenzaldehyde-S-benzylthiocarbazonate (BBTC) as ligand as well as its metal complexes against three Gram-positive and three Gram-negative bacteria.

EXPERIMENTAL

All the reagents used were of AnalaR grade. The precursor 2,4,5-trimethoxybenzaldehyde were procured from Lupin and S-benzylthiocarbamate was procured from Merck, India. The two precursors were condensed together to produce the required ligand according to the reported method [33]. 2,4,5-Trimethoxybenzaldehyde (0.01 mol, 1.96 g) and S-benzylthiocarbamate (0.01 mol, 1.98 g) were dissolved together in 30 mL of ethanol and about 2 mL of conc. H_2SO_4 was added. The resulting solution was refluxed on water bath using air condenser for about 4 h, where by yellow turbidity appeared which got solidified after leaving overnight (Scheme-I). The yellow solid was filtered and recrystallized in ethanol-acetone mixture and dried in desiccator on anhydrous CaCl_2 (Yield: 79 %, m.p. 184 °C).

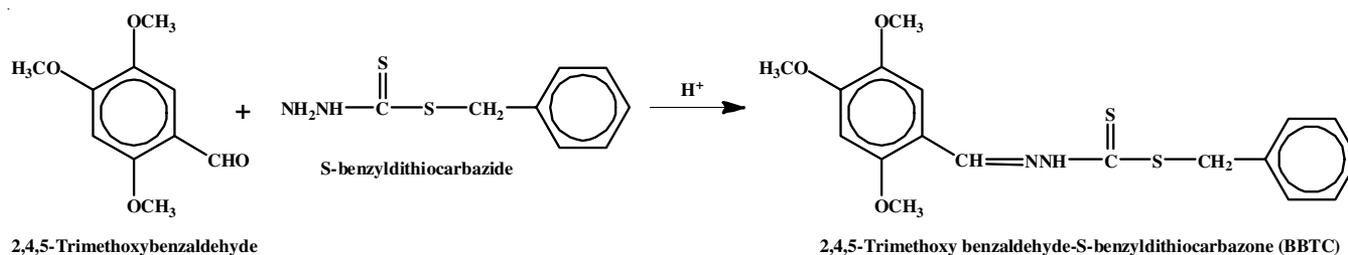
The ligand used for complexation with Mn(II), Fe(II) and Co(II) metal ions was done by refluxing method. The ligand as well as complexes were microanalyzed using Perkin-Elmer-2400-CHN elemental analyzer. The Mn(II) and Co(II) were estimated gravimetrically while Fe(II) was estimated volumetrically after decomposition of the complexes. The FTIR spectra of ligand and complexes were recorded on Perkin-Elmer-FTIR spectrometer using KBr as disc in the range of 4000-400 cm^{-1} . The magnetic susceptibility of complexes has been determined by Gouy's balance at room temperature using mercuric tetra-thiocyanatocobaltate(II) as calibrant. The electronic spectra

of metal complexes were recorded on Shimadzu UV-Visible spectrophotometer (UV-160). The molar conductivity of the complexes was determined in DMF solution (10^{-3} M) using Toshiniwal CL-01-06 conductivity bridge.

Antimicrobial activity: The ligand as well as its metal complexes were screened against three Gram-positive bacterial strains *viz.* *Staphylococcus aureus*, *Bacillus subtilis* and *Micrococcus luteus* and three Gram-negative bacterial strains *viz.* *Escherichia coli*, *Klebsiella pneumoniae* and *Proteus mirabilis*. The screening was carried out by agar well diffusion method. The assay was conducted by the use of MHA (Mueller Hinton Ager). Steryl cotton swabs were used to develop a uniform bacterial lawn. Each sample (1 mg) was dissolved in 1 mL of DMSO, which was used as control for antimicrobial study. The concentration of ciprofloxacin was taken as 1 mg/mL for standard. The plates containing bacterial strains were incubated for 24 h at 35 °C. The antibacterial activity of ligand and its complexes was determined by measuring the diameter of inhibition zone. All the tests were carried out in triplicate.

RESULTS AND DISCUSSION

The percentage composition of synthesized ligand and its metal(II) complexes has been given in Table-1. The extremely low value of conductivity ($18\text{-}23 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of M(II) complexes clearly indicates their non-electrolytic nature [34-36]. The percentage composition and molar conductivity



Scheme-I

TABLE-1
% COMPOSITION, PHYSICAL PROPERTIES AND MOLAR CONDUCTIVITY OF LIGAND AND ITS METAL(II) COMPLEXES

Compounds	Colour	m.p. (°C)	Yield (%)	Elemental analysis (%): Found (calcd.)						λ ($\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
				M	C	H	N	S	Cl	
BBTC (L)	Yellow	184	79.0	66.00 (65.85)	5.88 (6.09)	8.21 (8.54)	19.34 (19.51)	–	–	–
[Mn(BBTC) ₂ Cl ₂]	Magenta	265	72.0	6.82 (7.03)	55.84 (55.24)	4.91 (5.115)	7.00 (7.16)	16.14 (16.37)	8.91 (9.07)	21.00
[Mn(BBTC) ₂ (NO ₃) ₂]	Dull red	271	71.0	6.28 (6.59)	51.96 (51.74)	4.52 (4.979)	9.89 (10.06)	15.13 (15.33)	–	23.00
[Mn(BBTC) ₂ (CH ₃ COO) ₂]	Red	278	71.0	6.42 (6.63)	58.23 (57.90)	5.31 (5.54)	6.62 (6.75)	15.36 (15.44)	–	20.00
[Fe(BBTC) ₂ Cl ₂]	Brown	279	79.0	6.89 (7.15)	55.42 (55.17)	4.96 (5.11)	6.90 (7.15)	16.18 (16.34)	8.91 (9.07)	20.00
[Fe(BBTC) ₂ (NO ₃) ₂]	Dull brown	281	78.5	6.53 (6.74)	51.92 (51.67)	4.51 (4.75)	9.89 (10.06)	15.24 (15.31)	–	18.00
[Fe(BBTC) ₂ (CH ₃ COO) ₂]	Bright brown	269	79.0	6.58 (6.74)	57.96 (57.83)	5.39 (5.54)	6.61 (6.75)	15.34 (15.42)	–	20.00
[Co(BBTC) ₂ Cl ₂]	Light pink	280	79.0	7.38 (7.51)	55.21 (54.96)	4.89 (5.10)	6.92 (7.12)	16.04 (16.28)	8.86 (9.03)	21.00
[Co(BBTC) ₂ (NO ₃) ₂]	Pinkish	281	78.0	6.84 (7.03)	51.79 (51.50)	4.58 (4.77)	9.92 (10.01)	15.11 (15.26)	–	23.00
[Co(BBTC) ₂ (CH ₃ COO) ₂]	Sharp pink	281	80.0	6.88 (7.08)	57.82 (57.62)	5.39 (5.52)	6.52 (6.72)	15.21 (15.37)	–	23.00

BBTC = 2,4,5-Trimethoxy benzaldehyde-S-benzylthiocarbazon

of the metal complexes revealed their formation as $[ML_2X_2]$ where, M = Mn(II), Fe(II) and Co(II), L = BBTC ligand and X = Cl⁻, NO₃⁻ and CH₃COO⁻.

FTIR analysis: The free ligand absorbs at 3455 cm⁻¹, which is assigned to N-H stretching vibration [37-39] of the ligand and remains intact on complexation with metal ion. It indicates that nitrogen of the ligand is not involved in coordination. The free ligand absorbs at 2620 cm⁻¹ is due to $\nu(\text{CS-CH}_2)$ vibration, which doesn't undergo any change in complexes and also is an indicative of non-participation of thio-ether group of ligand in coordination. A medium band appears at 1650 cm⁻¹ undergoes a negative shift by 32-35 cm⁻¹ and appears at 1650-1615 cm⁻¹ in the FTIR spectra of complexes. It is a distinct indication of coordination through azomethine nitrogen of ligand in complexes [40-42]. The coordination through azomethine nitrogen of ligand is further supported by an increase by 15 cm⁻¹ in absorption frequency of N-N which absorbs at 1013 cm⁻¹ in FTIR spectrum of free ligand [43]. The methoxy group of free ligand absorbs at 1160 cm⁻¹ with medium intensity and remains almost intact in the spectra of complexes. It shows the non-participation of methoxy oxygen of ligand in coordination. The medium band appeared at 1045 cm⁻¹ is due to $\nu(\text{C=S})$ stretching vibration of free ligand, which undergoes red shift appearing at 1020-1010 cm⁻¹ in complexes, thus confirms a coordination through thionyl sulphur of ligand to the metal ions [44]. The coordination through sulphur and azomethine nitrogen of ligand is further supported by the appearance of

new band at 535-530 cm⁻¹ due to $\nu(\text{M-N})$ and 450-445 cm⁻¹ due to $\nu(\text{M-S})$ in the FTIR spectra of the complexes [45]. In addition to these bands some new bands also appeared in complexes. In complexes **1**, **4** and **7**, new band appears at 425-420 cm⁻¹ due to $\nu(\text{M-Cl})$ stretching showing the presence of chloride in the coordination sphere [46]. In complexes **2**, **5** and **8**, two new bands appear at 1384-1380 and 848-840 cm⁻¹, which shows the presence of mono coordinated NO₃⁻ ion in these complexes [47]. The new bands appeared at 1565-1560 and 1330-1320 cm⁻¹ in FTIR spectra of complexes **3**, **6** and **9** may be attributed to $\nu(\text{COO}^-)_{\text{asy}}$ and $\nu(\text{COO}^-)_{\text{sy}}$, respectively [48]. The $\Delta\nu$ between symmetric and asymmetric vibrations of acetate is more than 200 cm⁻¹, which is typical of monodentate coordination characteristic of acetate group in these complexes [49]. The key FTIR bands of ligand and complexes are presented in Table-2.

Magnetic moment and electronic spectra: Magnetic moment of Mn(II) complexes are found to be 5.80-5.83 B.M. These values are very close to the magnetic moment corresponding to five unpaired electrons. This is indicative of the fact that Mn²⁺ complexes are high spin magnetically dilute octahedral complexes [50]. The slightly low value of magnetic moment may be due to spin-orbit coupling, which further restricts the spin as well as orbital motion of electron to little extent. The Mn(II) complexes display four very weak bands in their electronic spectra. The electronic spectral bands data are given in Table-3. The weak bands of electronic spectra of

TABLE-2
KEY FTIR BANDS OF LIGAND AND ITS METAL(II) COMPLEXES (cm⁻¹)

Compounds	$\nu(\text{N-H})$	$\nu(\text{C-S-CH}_2)$	$\nu(\text{CH=N})$	$\nu(\text{C=S})$	$\nu(\text{N-N})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$	NO ₃ ⁻	CH ₃ COO ⁻
BBTC (L)	3455	2620	1650	1045	1030	-	-	-	-	-
[Mn(BBTC) ₂ Cl ₂]	3455	2620	1620	1015	1040	530	450	425	-	-
[Mn(BBTC) ₂ (NO ₃) ₂]	3450	2620	1620	1010	1040	530	450	-	1384} s 848} w	-
[Mn(BBTC) ₂ (CH ₃ COO) ₂]	3450	2620	1620	1010	1040	532	450	-	-	1560} m 1325} m
[Fe(BBTC) ₂ Cl ₂]	3452	2620	1618	1015	1048	530	445	425	-	-
[Fe(BBTC) ₂ (NO ₃) ₂]	3450	2620	1615	1020	1042	535	448	-	1380} s 840} w	-
[Fe(BBTC) ₂ (CH ₃ COO) ₂]	3455	2620	1620	1015	1040	535	448	-	-	1560} m 1330} m
[Co(BBTC) ₂ Cl ₂]	3455	2620	1615	1015	1042	530	445	420	-	-
[Co(BBTC) ₂ (NO ₃) ₂]	3455	2620	1615	1018	1042	535	445	-	1380} s 845} w	-
[Co(BBTC) ₂ (CH ₃ COO) ₂]	3450	2620	1617	1020	1040	535	445	-	-	1565} m 1320} m

TABLE-3
ELECTRONIC SPECTRAL BANDS (cm⁻¹) AND MAGNETIC MOMENT OF METAL(II) COMPLEXES OF
2,4,5-TRIMETHOXY BENZALDEHYDE-S-BENZYLTHIOCARBAZONE (BBTC)

Complexes	Manganese complex					Iron complex				Cobalt complex				
	Electronic spectral bands (cm ⁻¹)				μ_{eff} (B.M.)	Electronic spectral bands (cm ⁻¹)			μ_{eff} (B.M.)	Electronic spectral bands (cm ⁻¹)				μ_{eff} (B.M.)
	ν_1	ν_2	ν_3	ν_4		ν_1	ν_2	ν_3		ν_2	ν_3	ν_4	ν_5	
A	18100	24435	26400	27700	5.81	8450	14875	27720	5.10	7800	10,100	19,900	25,500	4.75
B	18050	24190	26300	27600	5.80	8570	15255	27570	5.00	7550	10,000	19,700	20,650	4.72
C	18200	24210	26150	27300	5.83	8510	15065	27210	5.00	8000	10,300	20,300	21,000	4.79

A = [M(BBTC)₂Cl₂]; B = [M(BBTC)₂(NO₃)₂]; C = [M(BBTC)₂(CH₃COO)₂] where M = Mn, Fe, Co

TABLE-4
DATA OF CRYSTAL FIELD PARAMETERS FOR Mn(II) COMPLEXES

Complexes	v_2/v_1	Dq (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)	C/B	β
[Mn(BBTC) ₂ Cl ₂]	1.35000	1254.442	896.030	3098.00	3.45413	6.66354
[Mn(BBTC) ₂ (NO ₃) ₂]	1.34017	1649.238	916.243	3005.51	3.28020	4.55795
[Mn(BBTC) ₂ (CH ₃ COO) ₂]	1.33022	1427.450	892.156	3057.68	3.42730	7.06699

Mn(II) complexes are assigned to the following spin forbidden transitions, $v_1 = {}^6A_{1g} \rightarrow {}^4T_{1g}$ (⁴G), $v_2 = {}^6A_{1g} \rightarrow {}^4T_{2g}$ or ${}^4A_{1g}$ or 4E_g (⁴G), $v_3 = {}^6A_{1g} \rightarrow {}^4E_g$ (⁴D) and $v_4 = {}^6A_{1g} \rightarrow {}^4T_{1g}$ (⁴P).

Using Tanabe-Sugano diagram, the values of different crystal field parameters have been derived and values are shown in Table-4. The ratio of Racah parameter C/B derived for Mn(II) complexes (3.28-3.45) is very close to the theoretical value (3.5) [51]. The values of different crystal field parameters support octahedral geometry around Mn(II) in these complexes [36,52].

The magnetic moment of Fe(II) complexes exhibit magnetic moment 5.00-5.10 B.M., which shows the presence of four unpaired electrons in the complexes. The values are a bit higher than that corresponding to four unpaired electrons (4.89 B.M.), which may be attributed to the ground state term ⁵T_{2g} being orbitally degenerate contributes to the magnetic moment of six coordinated Fe(II) complexes. The magnetic moment of six coordinate Fe(II) complexes also show enhancement due to deviation from octahedral symmetry [53-55]. The Fe(II) complexes display three bands in their electronic spectra, which is an indicative of tetragonal distortion in octahedral symmetry of Fe(II) complexes. Under the influence of tetragonal distortion, both the ground state crystal field terms ⁵T_{2g} and the excited crystal field term ⁵E_g of its ground term ⁵D undergo further splitting causing the possibility of three spin allowed transition bands. The electronic spectral bands [56] and their assignment are shown in Table-3. These bands were assigned to the following spin allowed transitions, $v_1 = {}^5E_g \rightarrow {}^5B_{2g}$, $v_2 = {}^5E_g \rightarrow {}^5A_{1g}$ and $v_3 = {}^5E_g \rightarrow {}^5B_{1g}$. On the basis of these transitions and energy associated with different transitions, the various crystal field parameters have been derived and values are presented on Table-5.

TABLE-5
DATA OF VARIOUS CRYSTAL FIELD
PARAMETER OF Fe(II) COMPLEXES

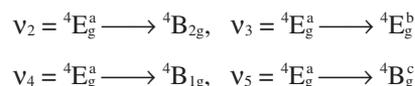
Complexes	Dq _(xy) (cm ⁻¹)	Dq _(z) (cm ⁻¹)	D _s (cm ⁻¹)	D _t (cm ⁻¹)
[Fe(BBTC) ₂ Cl ₂]	1927	1690.40	3042.00	135.2
[Fe(BBTC) ₂ (NO ₃) ₂]	1900	1766.72	2983.60	76.16
[Fe(BBTC) ₂ (CH ₃ COO) ₂]	1870	1750.00	2950.70	68.42

From Table-5, it is obvious that Dq_(z) for all the complexes is less than Dq_(xy), which shows that the axial ligands are slightly away from the metal ion in respect of the planer ligands in all the complexes. Hence, tetragonally elongated octahedral symmetry (D_{4h}) for all the Fe(II) complexes is predicted. The elongation along z-axis is further supported by the positive value of the radial integral D_t for all the Fe(II) complexes [31].

Electronic spectra of Co(II) complexes: The magnetic moment of Co(II) complexes has been found 4.72-4.79 B.M. Co(II) is a d⁷ system having three unpaired electrons and hence the spin only value of magnetic moment is expected to be 3.87

B.M. An abnormality in the magnetic moment of Co(II) complexes may be attributed to ⁴T_{1g} ground state crystal field term in octahedral symmetry which appreciably contribute to the magnetic moment of Co(II) complexes in octahedral symmetry [29,57,58]. The electronic spectral band and magnetic moment of Co(II) complexes are given in Table-3.

The bands have been assigned to the following spin allowed transitions:



The first band v_1 is due to ${}^4E_g^a \longrightarrow {}^4A_{2g}$ is not observed due to small gap between the two levels causing absorption energy in infrared range. The value of 10Dq_(xy) has been derived from $v_4 - v_2$ and D_t has been derived from 4/35 ($v_3 - v_2$), Dq_(xy) was derived from the popular equation, $D_t = 4/7 (Dq_{(xy)} - Dq_{(z)})$. The values of different crystal field parameters derived from the spectral bands are shown in Table-6.

TABLE-6
DATA OF VARIOUS CRYSTAL FIELD
PARAMETER OF Co(II) COMPLEXES

Complexes	Dq _(xy) (cm ⁻¹)	Dq _(z) (cm ⁻¹)	D _t (cm ⁻¹)	D _s (cm ⁻¹)
[Co(BBTC) ₂ Cl ₂]	1.210	748	264	3,754
[Co(BBTC) ₂ (NO ₃) ₂]	1.215	725	280	3,725
[Co(BBTC) ₂ (CH ₃ COO) ₂]	1.230	770	263	3,821

From D_s and D_t values, the value of v_1 has been derived and found in 6,694-6,919 cm⁻¹ region, which falls in infrared region. The positive value of D_t and D_s are the indicative of tetragonally elongated octahedral geometry of all the Co(II) complexes [59,60]. The tetragonal elongation along z-axis in all Co(II) complexes is also supported by the smaller value of Dq_(z) than Dq_(xy) [61].

Antimicrobial activity: Table-7 clearly indicates that free ligand as well as its metal complexes are active against all the bacteria, moreover, all the complexes are more active than the ligand. The enhanced microbial activity of complexes and the ligand may be explained using chelation effect theory [62-64]. However, the activity of ligand and its metal complexes is less than that of standard *i.e.* ciprofloxacin.

Conclusion

Schiff base 2,4,5-trimethoxy benzaldehyde-S-benzylidithiocarbazone (BBTC) ligand is found to act as neutral bidentate coordinated through azomethine nitrogen and thionic sulphur. The positions along z-axis are occupied by chloride or nitrate or acetate ions. All the complexes of Mn(II), Fe(II) and Co(II) are found to possess D_{4h} symmetry with elongation along z-axis. The free ligand and its complexes are found most active against *E. coli* and *S. aureus*.

TABLE-7
ZONE OF INHIBITION OF LIGAND AND COMPLEXES (mm)

Test compound	Gram-negative bacteria			Gram-positive bacteria		
	<i>E. coli</i>	<i>K. pneumoniae</i>	<i>P. mirabilis</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>M. luteus</i>
L	25.0	22.0	20	26.0	25.0	25.0
[Mn(L) ₂ Cl ₂]	24.6	28.0	25	42.0	30.0	29.0
[Mn(L) ₂ (NO ₃) ₂]	33.0	28.7	29	37.0	29.0	29.8
[Mn(L) ₂ (CH ₃ COO) ₂]	29.0	26.0	28	31.0	29.6	28.0
[Fe(L) ₂ Cl ₂]	31.0	30.0	31	34.0	32.0	33.0
[Fe(L) ₂ (NO ₃) ₂]	30.8	29.6	30	32.0	32.0	30.0
[Fe(L) ₂ (CH ₃ COO) ₂]	28.9	30.0	30	30.0	31.0	32.0
[Co(L) ₂ Cl ₂]	26.4	25.0	24	29.0	28.0	28.0
[Co(L) ₂ (NO ₃) ₂]	26.0	24.8	24	28.8	29.0	27.0
[Co(L) ₂ (CH ₃ COO) ₂]	26.0	27.0	25	28.6	27.0	29.0
Ciprofloxacin control	35.0	36.0	35	34.0	34.0	36.0

ACKNOWLEDGEMENTS

One of the authors, Deepak Kumar is thankful to University Grants Commission for granting Rajiv Gandhi National Fellowship vide registration no.: RGNF-2017-18-SC-BIH-41422.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- J.P. Holland, F.I. Albrithio, H.M. Betts, P.D. Bonnitcha, P. Burka, M. Christlieb, G.C. Churchill, A. R. Cowly, J.R. Dilworth, P.S. Donnelly, J.C. Green, J.M. Peach, S.R. Vasudevan and J.E. Warren, *Inorg. Chem.*, **46**, 465 (2007); <https://doi.org/10.1021/ic0615628>.
- M.C. Rodríguez-Argüelles, P. Tourón-Touceda, R. Cao, A.M. Garcia-Deibe, P. Pelagatti, C. Pelizzi and F. Zanie, *J. Inorg. Biochem.*, **103**, 35 (2009); <https://doi.org/10.1016/j.jinorgbio.2008.08.015>.
- M. Tayagi and S. Chandra, *J. Indian Chem. Soc.*, **89**, 147 (2012).
- R. B. Singh, B. S. Garg and R. P. Singh, *Talanta*, **23**, 619 (1978); [https://doi.org/10.1016/0039-9140\(78\)80163-5](https://doi.org/10.1016/0039-9140(78)80163-5).
- K.H. Reddy and D. Venkatarreddy, *Q. Chem. Rev.*, **1**, 47 (1985).
- B.S. Garg and V.K. Jain, *Microchem. J.*, **38**, 144 (1988); [https://doi.org/10.1016/0026-265X\(88\)90017-3](https://doi.org/10.1016/0026-265X(88)90017-3).
- N.B.L. Prasad, K.H. Reddy and T.S. Reddy, *Indian J. Chem.*, **42A**, 112 (2003).
- K.H. Reddy, N.B.L. Prasad, T.S. Reddy and N.S. Rao, *J. Indian Chem. Soc.*, **83**, 980 (2006).
- V.S. Basha and K.H. Reddy, *J. Indian Chem. Soc.*, **91**, 823 (2014).
- R. Poschke, S. Hiebdch, C. Tschierske, M.A. Oakley and E. Sinn, *Inorg. Chim.*, **2**, 8230 (2003); <https://doi.org/10.1021/ic0301021>.
- K. Drabente, A. Bioloska and Z. Ciunik, *Inorg. Chim. Commun.*, **7**, 224 (2004); <https://doi.org/10.1016/j.inoche.2003.11.008>.
- X.B. Arion, E. Peisner, N. Fremuth, M.A. Jokapec, B. Keppler, V.Y. Kukushin and A.J.L. Pombeiro, *Inorg. Chim.*, **42**, 6024 (2003); <https://doi.org/10.1021/ic034605i>.
- S.N. Pandeya, D. Sriram, G. Nath and E.D. Clercq, *Il Pharmaco*, **54**, 624 (1999); [https://doi.org/10.1016/S0014-827X\(99\)00075-0](https://doi.org/10.1016/S0014-827X(99)00075-0).
- A.D. Nayak, S.M. Annigeri, U.B. Gangadharmath, B.K. Revankar, V.B. Mahale and V.K. Reddy, *Indian J. Chem.*, **49A**, 2046 (2003).
- R.N. Patel, V.P. Sondhiya, K.K. Shukla, D.K. Patel, Y. Singh and R. Pandey, *J. Indian Chem. Soc.*, **89**, 1085 (2012).
- M. Bedi, S. Sharma, S. Barshney and A.K. Varshney, *J. Indian Chem. Soc.*, **89**, 309 (2012).
- N. K. Singh and A. Srivastava, *Transition Met. Chem.*, **25**, 133 (2000); <https://doi.org/10.1023/A:1007081218000>.
- A.E. Graminha, C. Rodrigues, A.A. Batista, L.P. Teixeira, E.S. Fagundas and H. Beraldo, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **69**, 1073 (2008); <https://doi.org/10.1016/j.saa.2007.06.005>.
- S.A. Khan and M. Yusuf, *Eur. J. Med. Chim.*, **44**, 2270 (2009); <https://doi.org/10.1016/j.ejmech.2008.06.008>.
- V.S. Shekhawat, S. Varshney and A.K. Varshney, *J. Indian Chem. Soc.*, **94**, 21 (2017).
- E. Hossain, M. Alam, M. Ali, M. Nazimuddin, E. Smith and C. Hynes, *Polyhedron*, **15**, 973 (1996); [https://doi.org/10.1016/0277-5387\(95\)00310-X](https://doi.org/10.1016/0277-5387(95)00310-X).
- M. Tarafder, T.J. Khoo, A. Crouse, M. Ali, B. Yamin and H. Fun, *Polyhedron*, **21**, 2691 (2002); [https://doi.org/10.1016/S0277-5387\(02\)01272-X](https://doi.org/10.1016/S0277-5387(02)01272-X).
- F. How, A. Crouse, M. Tahir and D. Watkin, *J. Chem. Crystallogr.*, **39**, 894 (2009); <https://doi.org/10.1007/s10870-009-9586-0>.
- A.K. Mukhopadhyay, *Industrial Chemical Cresols and Downstream Derivations*, CRC Press: New York, p. 81 (2004).
- S. Salunke-Gawali, E. Pereira, U. Ali and D.S. Bhand, *J. Mol. Struct.*, **1148**, 435 (2017); <https://doi.org/10.1016/j.molstruc.2017.06.130>.
- S. Reddy, Susheela and Jayatagaraju, *Indian J. Chem.*, **43A**, 341 (2004).
- S. Alvarez, *Chem. Rev.*, **115**, 13447 (2015); <https://doi.org/10.1021/acs.chemrev.5b00537>.
- C.S. Dilip, V. Thangaraj and A.P. Raj, *Arab. J. Chem.*, **9(Suppl.1)**, S731 (2016); <https://doi.org/10.1016/j.arabjc.2011.07.016>.
- N. Sinha, S. Kumar, D. Kumar, C. M. Chandra, S. Kumar and S. Sharma, *Asian J. Chem.*, **30**, 2424 (2018); <https://doi.org/10.14233/ajchem.2018.21429>.
- S. Kumar, P. K. Pandey, N. Sinha, S. Chaudhry and S. Sharma, *J. Phys. Sci.*, **29**, 1 (2018); <https://doi.org/10.21315/jps2018.29.3.1>.
- P. Pradhan, S.K. Sinha, P. Verma, S. Kumar and S. Sharma, *Asian J. Chem.*, **30**, 1989 (2018); <https://doi.org/10.14233/ajchem.2018.21362>.
- V. Kumar, P.K. Singh, V. Kumari, B. Kumar and S. Sharma, *Orient. J. Chem.*, **34**, 1937 (2018); <https://doi.org/10.13005/ojc/3404030>.
- M.A.A.A. Islam, M.C. Sheiks, N.A. Mumit, P. Miyatake, M.A. Alam and M.O.A. Mondan, *J. Coord. Chem.*, **69**, 3580 (2016); <https://doi.org/10.1080/00958972.2016.1233329>.
- B.B. Mahapatra, A.K. Sarangi and P.P. Mishra, *J. Indian Chem. Soc.*, **93**, 9 (2016).
- B. Kumari, B. Kumar, S. Kumar, D. Kumar and S. Sharma, *Int. J. Eng. Sci. Inv.*, **7**, 14 (2018).
- B. Kumar, B. Kumar, S. Kumar, D. Kumar and S. Sharma, *Orient J. Chem.*, **33**, 2643 (2017); <https://doi.org/10.13005/ojc/330563>.
- R.B. Singh and S. Srivastava, *J. Indian Chem. Soc.*, **90**, 711 (2013).
- K.V. Sharma, V. Sharma and U.N. Tripathi, *J. Coord. Chem.*, **62**, 506 (2009); <https://doi.org/10.1080/00958970802233110>.

39. S. Bharti, M. Chaudhry, S.P. Rawat, Sangeeta, N.K. Ahmad, S.P. Sharma, S.S. Shaket, B. Singh, B. Das and S. Kumar, *J. Indian Chem. Soc.*, **93**, 953 (2015).
40. S. Chandra and K.K. Sharma, *Transition Met. Chem.*, **8**, 1 (1983); <https://doi.org/10.1007/BF00618784>.
41. K.C. Raja, N.T. Madhu and P.K. Radhakrishnan, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 115 (2002).
42. N. Gayatri and M.S. Suresh, *Asian J. Chem.*, **29**, 541 (2017); <https://doi.org/10.14233/ajchem.2017.20227>.
43. R. Ezhilarsi, J.H. Malarkodi and S. Divya, *Asian J. Chem.*, **29**, 2619 (2017); <https://doi.org/10.14233/ajchem.2017.20730>.
44. S.S. Garje and V.K. Jain, *Coord. Chem. Rev.*, **236**, 35 (2003); [https://doi.org/10.1016/S0010-8545\(02\)00159-5](https://doi.org/10.1016/S0010-8545(02)00159-5).
45. U.N. Tripathi, J. Solanki, A. Bhardwaj and T.R. Thapak, *J. Coord. Chem.*, **61**, 4025 (2008); <https://doi.org/10.1080/00958970802199964>.
46. S. Nandi, S. Roy, K. Das, A. Datta and C. Sinha, *J. Indian Chem. Soc.*, **93**, 1253 (2016).
47. S.A. Canron and S. Brooker, *Inorg. Chem.*, **50**, 3697 (2011); <https://doi.org/10.1021/ic200059n>.
48. G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980); [https://doi.org/10.1016/S0010-8545\(00\)80455-5](https://doi.org/10.1016/S0010-8545(00)80455-5).
49. T. Ghose, S. Bhattacharya and G.N. Mukherjee, *J. Indian Chem. Soc.*, **81**, 449 (2004).
50. F. A. Cotton Progress in inorganic Chemistry, InterScience Publishers, vol. 6, p. 43 (1964).
51. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier: New York, edn 2, p. 90 (1984).
52. M.R. Sibappa, C. Basavaraj, S. Weesh and S.D. Agundi, *J. Indian Chem. Soc.*, **86**, 197 (2009).
53. F.E. Mabbs and D.J. Machin, *Magnetism and Transition metal Complexes*, Chapman & Hall: London, p. 159 (1973).
54. H. Montgomery, R.V. Chastain, J.J. Natt, A.M. Witkouska and E.C. Ligafelter, *Acta. Cryst.*, **22**, 715 (1967); <https://doi.org/10.1107/S0365110X67001550>.
55. W.C. Hammiton, *Acta. Cryst.*, **15**, 353 (1962); <https://doi.org/10.1107/S0365110X62000870>.
56. A.B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier: New York, edn 2, p. 26 (1984).
57. B.N. Figgis, *Introduction to Ligand Fields*, Wiley Eastern Limited: New Delhi, p. 261, 267 (1964).
58. S. Roy, A.K. Maji, D. Sutradhar, S. Chaubey, R. Ghose and B.K. Ghose, *J. Indian Chem. Soc.*, **92**, 1387 (2015).
59. A.B.P. Lever, I.M. Walker and P.J. McCarthy, *Inorg. Chim. Acta*, **39**, 81 (1980); [https://doi.org/10.1016/S0020-1693\(00\)93639-9](https://doi.org/10.1016/S0020-1693(00)93639-9).
60. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier: New York, edn 2, pp. 484-485 (1984).
61. S.K. Tripathi, P. Panda, P.K. Das, N.K. Behra and A.K. Panda, *J. Indian Chem. Soc.*, **93**, 275 (2016).
62. S.K. Sengupta, O.P. Pandey, B.K. Srivastava and V.K. Sharma, *Transition Met. Chem.*, **23**, 349 (1998); <https://doi.org/10.1023/A:1006986131435>.
63. B.G. Tweedy, *Phytopathology*, **55**, 910 (1964).
64. S.B. Kalia, G. Kaushal, M. Kumar, S.S. Cameotra, A. Sharma, M.L. Verma and S.S. Kanwar, *Braz. J. Microbiol.*, **40**, 916 (2009); <https://doi.org/10.1590/S1517-83822009000400024>.