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SYNTHESIS AND STRUCTURAL STUDIES OF COMPLEXES OF Cu (II), Ni (II) AND Co (II) WITH 2'-HYDROXY CHALCONES

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ABSTRACT

Complexes of Cu (II), Ni (II) and Co (II) with 1-(2'-hydroxy-3'-iodo-5'-chlorophenyl]-3-(3,4-methylenedioxyphenyl)-2-propen-1-one (L_1), 1-(2'-hydroxy-3'-iodo-5'-bromophenyl]-3-(3,4-methylenedioxyphenyl)-2-propen-1-one (L_2) and 1-(2'-hydroxy-3'-bromo-4'-methyl-5'-chlorophenyl]-3-(3,4-methylenedioxyphenyl)-2-propen-1-one (L_3) have been synthesized and characterized by analytical, molar conductivity, magnetic, IR, electronic spectra, TGA and ^{1}H NMR spectra. Electronic spectral data suggest that all Cu (II) complexes are square planar and all Ni (II) and Co (II) complexes are having octahedral geometry.

Key words: Metal complexes, IR, Electronic spectra, TGA, ^{1}H NMR spectra.

INTRODUCTION

Biological active 2'-hydroxychalcone ligands coordinating through carbonyl and enolic oxygens are reported to be mononegative bidentate towards Cu (II)[1]. 2'-Hydroxychalcones possess wide range of biological activity such as antibacterial[2], antifungal[3], anticancer[4], antimitotic[5], antitubercular[6], antiviral[7], and antiulcer[8], aldose reductase inhibitors i.e. antidiabetic agents[9] and antimalarial[10]. In recent years, chalcones possessing inhibitory effect on Rat Lens Aldoxe Reductase [RLAR] and Rat Platelet Aggregation[11] were studied. 2'-Hydroxychalcone were employed as analytical reagents for some metal ions[12].

The literature survey reveals that there are very few papers on complexes of Cu (II), Ni (II) and Co (II) of 2'-hydroxychalcones. Therefore, it was thought worthwhile to

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*Author for correspondence; Mo.: +91 2469223132; E-mail: Khushalgk@rediffmail.com undertake the synthesis and characterization of Cu (II), Ni (II) and Co (II) complexes of 1-(2'-hydroxy 3',5'-substituted phenyl)-3-(3, 4-methylene- dioxyphenyl)-2-propene-1-one.

EXPERIMENTAL

All the chemicals used were of analytical grade. The 2'-hydroxychalcone (L_1, L_2 and L_3) were prepared by reacting piperonal (3,4-methylenedioxybenzaldehyde) with substituted acetophenone according to a method reported in the literature[13].

Synthesis of metal complexes

In the synthesis of all the Cu (II), Ni (II) and Co (II) complexes, the ligand (0.02 mole) in 50 mL methanol was treated with equimolar solution of 1 M NaOH[14] and refluxed on water bath for 15 minute. Then (0.01 M) metal salt in 10 mL methanol was added with constant stirring in all the cases. The ligand concentration was in slight excess of the 1 : 2 metal-ligand molar ratio. The reaction mixture was refluxed continuously on a water bath for 2 hrs. The solid mass separated was filtered through a sintered glass crucible (G_4) and the residue was washed several times with hot methanol until the washing were free of the excess of ligand. These complexes were finally dried under vacuum desiccator over fused $CaCl_2$ Analytical data are presented in Table 1. Conductance measurements were carried out in 10^{-3} M in DMF solution using a Elico digital conductometer model-180.

The magnetic susceptibility measurements of the complexes in the solid state were made on Guoy balance at room temperature using Hg $[Co(NCS)_4]$ as a standard. Diamagnetic corrections were applied using Pascal's constant. The IR-spectra of the metal complexes in KBr pellets in the range 4000-350 cm^{-1} were recorded making use of a Perkin-Elmer Infrared Spectrophotometer. UV-visible spectra in DMF were recorded on a Shimadzu multipurpose recording spectrophotometer model 1601. TG and DTA analyses of metal complexes were carried out in nitrogen atmosphere in the range 25-1200^{o}C on Shimadzu DTG-50 with a heating rate 10^{o}C min^{-1} using alumina as a standard.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature, insoluble in water, and many of the common organic solvents but soluble in DMF and DMSO. The analytical data of the complexes (Table 1) indicate that their stoichiometry may be represented as 1 : 2 metal to ligand ratio. The complexes of Ni (II) and Co (II) with all ligands are also further associated with two moles of water molecules, which is confirmed by TGA. The molar conductance values of the complexes in DMF solvents are in the range 6.42 to 26.25 ohm^{-1} cm^2 mol^{-1} suggesting their non-ionic nature[15].

Infrared spectra

The free ligand showed a weak broad band around 3000-3100 cm^{-1}, but the IR spectra of Ni (II) and Co (II) complexes exhibited intense broad band near 3300-3400 cm^{-1} due to νOH of coordinated water molecules.

In the IR spectra of all the ligands, an intense band appearing around 1633 cm^{-1} is attributed to ν C = O. This band is shifted to lower wave numbers in the spectra of the complexes indicating coordination through oxygen of C = O group. The medium intensity band appearing around 1565 cm^{-1} in the ligands and the complexes are assigned to ν C = C (aromatic). The free ligand band at 1377 cm^{-1} was not observed in the complexes indicating the deprotonation of phenolic -OH of the ligands. Further ν C-OH intense band at around 1251 cm^{-1} observed in the ligand was shifted to lower frequency due to bonding to the metal ion. The ν M-O bond was observed in the complexes around 450 cm^{-1} [16].

Magnetic moments

The experimental magnetic moments of all the complexes are given in Table 1. The values obtained for the complexes of Cu (II) are in the range of 1.76-1.85 B.M. expected for square planar geometry[16,17] and for the complexes of Co (II)[18,19] and Ni (II)[19,20] are in the ranges of 4.66-5.02 B.M. and 2.86-3.13 B.M., respectively expected for octahedral geometry.

Electronic spectra

The electronic spectra of all the Co (II) complexes show two bands in the regions 13390-13850 cm^{-1} and 22500-22988 cm^{-1} ^4T_1g (F) → ^4A_2g (F), (V_2) and ^4T_1g (F) → ^4T_1g (p) (V_3) transitions, respectively in an octahedral geometry around Co(II).[19,21,23] and Ni (II) complexes exhibit two bands in the regions 13315-13550 cm^{-1} and 24270-25060 cm^{-1} ^3A_2g (F) → ^3T_1g (F), (V_2) and ^3A_2g (F) → ^3T_1g (p)[19] (V_3), respectively in an octahedral geometry around Ni (II)[14,24].

The electronic spectra of Cu (II) complexes show bands in the regions 13280-13386 cm^{-1} and 24965 – 25700 cm^{-1} [1], which may be assigned to the transitions ^2B_1g → ^2B_2g and ^2B_1g → ^2Eg, respectively assuming a square planar geometry[1,25].

The appearance of the third band around 37453 cm^{-1} may be attributed to the charge transfer phenomenon.

Electronic spectral data of complexes

S. No.	V_2 (cm^{-1})	V_3 (cm^{-1})	B (cm^{-1})	10 Dq (cm^{-1})	β	LFSE (Kcal/mol)
Co $(L_1)_2 (H_2O)_2$	13390	22172	718	8260	0.74	23.54
Co $(L_2)_2 (H_2O)_2$	13850	22988	744	8560	0.77	24.40
Co $(L_3)_2 (H_2O)_2$	13717	22500	710	8520	0.73	24.28
Ni $(L_1)_2 (H_2O)_2$	13315	25060	982	7850	0.94	22.49
Ni $(L_2)_2 (H_2O)_2$	13550	24270	899	8090	0.86	23.18
Ni $(L_3)_2 (H_2O)_2$	13425	24813	945	8030	0.91	23.00
Cu $(L_1)_2$	13386	25700	--	--	--	--
Cu $(L_2)_2$	13280	25180	--	--	--	--
Cu $(L_3)_2$	13351	24965	--	--	--	--

Various ligand field parameters such as the ligand field splitting energy (10 Dq), Racah inter-electronic repulsion parameter (B), covalent factor (β) and ligand field stabilization energy (LFSE) have been calculated for all the complexes of Co (II) and Ni (II) of all ligands[26,27].

The calculated Dq values of Co (II) and Ni (II) complexes suggest for the ligands a place between water and ammonia in the spectrochemical series. The B-values for the complexes are lower than free ion values, which indicates the orbital overlap and delocalization of d-orbital. The β-values obtained are less than one suggesting the considerable covalent character of the metal ligands bonds.

^{1}H NMR spectral study of Cu (II) and Ni (II) complexes

The ^{1}H NMR spectra of Cu (II) and Ni (II) complexes were recorded in $CDCl_3$ solvent. The position of each proton signal alongwith the chemical shift (δ ppm) is given in Table 1. ^{1}H NMR spectra of ligand and corresponding Cu (II) and Ni (II) complexes are shown in Figs. 1-3. ^{1}H NMR spectra are examined and chemical shifts in δ ppm for various protons are measured with respect to tetramethyl silane (TMS) as standard.

The ^{1}H NMR spectra of [Cu $(L_3)_2$] and [Ni $(L_3)_2 (H_2O)_2$] complexes and ligand are observed as well resolved peaks. The singlet observed at δ 2.34 due to three protons of methyl group and at δ 6.05 due to two proton of methylene group. The doublets was observed at δ 7.21 due to one proton of H_α and δ 7.68 due to one proton of H_α. The aromatic protons appeared as multiplets in the range of δ 6.85-7.90.

In the ^{1}H NMR spectra of Cu (II) complex, the signal due to OH proton (phenolic) is absent, which has appeared at δ 13.67 in ligand suggesting the deprotonation of phenolic group attached to benzene ring in 2'-hydroxychalcone. The interpretation of ^{1}H NMR spectrum of Cu (II) complex confirms the coordination of the ligand to the metal ion through phenolic oxygen atom.

In the ^{1}H NMR spectrum of Ni (II) complex also the signal due to OH proton (phenolic) is absent, suggesting the deprotonation of phenolic group attached to benzene ring in the 2'-hydroxychalcone. The interpretation of ^{1}H NMR spectra of Ni (II) complex, confirms the coordination of the ligand to the metal ion through phenolic oxygen atom. The broad signal at δ 3.00 is due to proton of coordinated water[28].

Table 1: ^{1}H NMR spectral data of ligand and it's Cu complex

Ligand	Cu-complex
δ 2.34 (s, 3H, Ar-CH_3)	2.62 (s, 3H, Ar-CH_3)
6.05 (s, 2H, CH_2)	6.60 (s, 2H, CH_2)
6.85-7.90 (m, 4H, Ar-H)	6.90-7.90 (m, 4H, Ar-H)
7.21 (d, 1H, H_α)	7.21 (d, 1H, H_α)
7.68 (d, 1H, H_β)	7.50 (d, 1H, H_β)
13.67 (s, 1H, Ar-OH)	absent

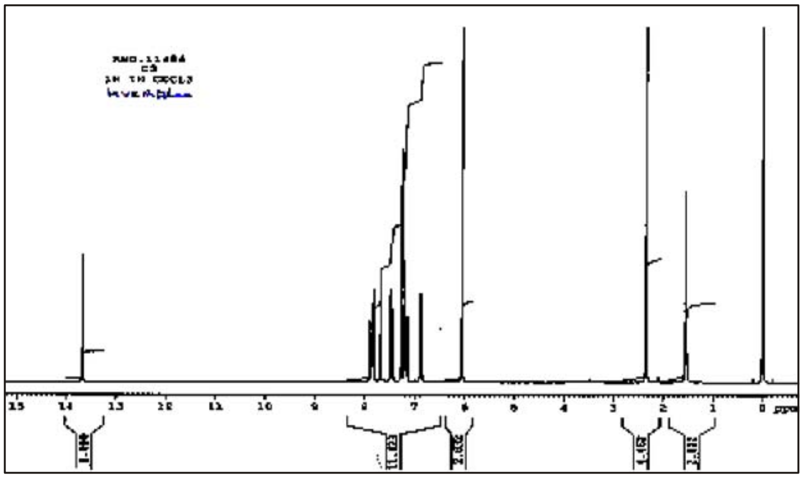


Fig. 1: ^{1}H NMR Spectrum of ligand (L_β)

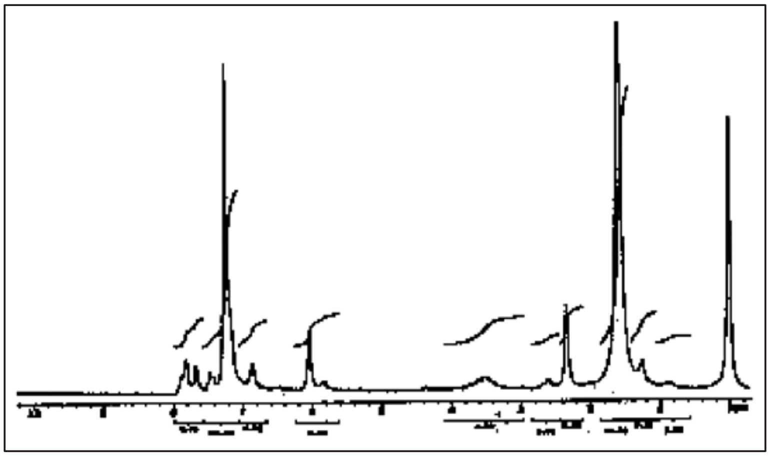


Fig. 2: ^{1}H NMR Spectrum of $[Cu(L_3)_2].H_2O$

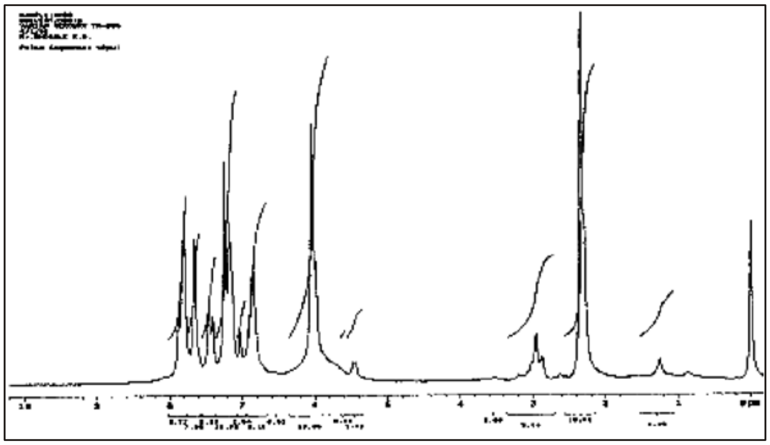


Fig. 3: ^{1}H NMR spectrum of $[Ni (L_3)_2 (H_2O)_2]$

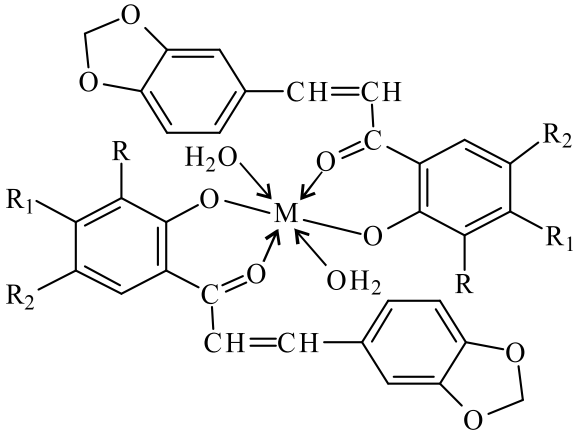
Table 2: ^{1}H NMR spectral data of ligand and it's Ni complex

Ligand	Ni (II) complex
δ 2.34 (s, 3H, Ar-CH_3),	δ 2.25 (s, 3H, Ar-CH_3),
6.05 (s, 2H, CH_2)	6.05 (s, 2H, CH_2)
6.85-7.90 (m, 4H, Ar-H)	6.90-7.90 (m, 4H, Ar-H)
7.21 (d, 1H, $H_α$),	7.30 (d, 1H, $H_α$),
7.68 (d, 1H, $H_β$),	7.50 (d, 1H, $H_β$)
13.67(s, 1H, Ar-OH)	3.00 (s, 1H, 4H, $2H_2O$)

Thermal analysis

Existence of coordinated water molecules in complexes is confirmed by TGA studies. Representative [Ni $(L_1)_2(H_2O)_2$] complex is stable upto 230°C and thereafter, it registers a mass loss of 3.54% (cal 3.91%), which corresponds to the loss of two coordinated water molecule. After 275°C, the anhydrous complex starts decomposing. Total mass loss up to 740°C was found to be 88.62% (cal. 87.97), which shows the formation of NiO. Finally, the residue left after 740°C is 7.84% (cal. 8.12%), which resembles the theoretical values. Hence from TGA, it is clear that the complex under study contains two water molecules, which are coordinated to central metal ion[29]. On the basis of the above discussion, complexes [Ni $(L_3)_2$ $(H_2O)_2$] may be assigned structure-1.

This structure is supported by magnetic moment and electronic spectral data.



Structural Formula - 1 M = Ni (II)

Complex No.	R	R_1	R_2
1	I	H	CH_3
2	Br	H	Cl
3	I	CH_3	Cl

The thermogram of [Cu $(L_3)_2$].H_2O show that the complex starts decomposing gradually, till it attains the temperature corresponding to 60-105°C, which corresponds to one mole of hydrated water. The loss of hydrated water molecule in Cu (II) complex is a single step process indicated by endothermic peak.

Table 2:

Metal complex	Temperature (^{o}C)	Wt. loss in %	Fragment removed
		Found (Calc.)	
[Ni $(L_3)_2(H_2O)_2$]	230	3.54 (3.91)	Two water molecule
	740	88.62 (87.97)	Organic part
	> 740	7.84 (8.12)	Metal oxide

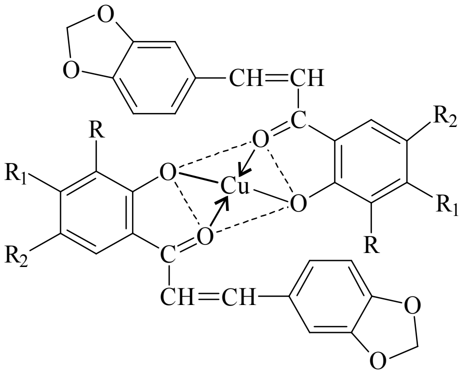
Table 3: Magnetic, conductivity and analytical data of Co (II), Ni (II) and Cu (II) complexes

Molecular formula	Colour	M.P./D. P. (^{o}C)	Yield (%)	Elemental analysis		Molar conductivity (ohm^{-1} cm^2 mol^{-1} x 10^{-3})	$\mu_{eff.}$ B.M.
				Halogen found (Calc.)	Metal found (Calc.)		
$C_{32}H_{22}O_{10}Cl_2I_2Co$	Reddish brown	234	70	34.40 (34.21)	6.82 (6.20)	8.05	4.66
$C_{32}H_{22}O_{10}Br_2I_2Co$	Reddish brown	212	65	40.10 (39.85)	5.78 (5.67)	18.75	5.02
$C_{34}H_{28}O_{10}Br_2Cl_2Co$	Brown	275	68	26.00 (26.13)	6.90 (6.67)	13.75	4.93
$C_{32}H_{22}O_{10}Cl_2I_2Ni$	Orange	240	72	34.00 (34.23)	6.42 (6.17)	23.75	3.01
$C_{34}H_{28}O_{10}Br_2I_2Ni$	Orange	208	72	39.52 (39.86)	5.90 (5.64)	16.25	2.86
$C_{34}H_{26}O_{10}Br_2Cl_2Ni$	Orange	300	75	26.35 (26.14)	6.45 (6.63)	21.25	3.13
$C_{32}H_{18}O_8Br_2I_2Cu$	Brown	250	76	35.90 (35.38)	6.64 (6.92)	20.0	1.77
$C_{34}H_{24}O_8Br_2I_2Cu$	Brown	240	72	41.25 (41.09)	6.11 (6.31)	16.25	1.85
$C_{34}H_{22}O_8Br_2Cl_2Cu$	Yellow	280	70	26.90 (27.10)	8.08 (7.46)	8.75	1.76

After this, Cu (II) complex shows sharp decrease in weight, indicating decomposition of complex. It is further confirmed by observing the endothermic nature of peak obtained in DTA curve. Organic part contents from the Cu (II) complex are found to be 91.26 %, which is comparative to theoretical value 90.66 %. The horizontal nature of the curve indicates the presence of thermally stable residual metal oxide (CuO)[27]. The percentage weight of the residual metal oxide are found to be 8.74 %, which is very close to the theoretical value 9.34%.

Thermal analysis supported to our findings from IR data in which, hydrated water molecule per mole of metal complex is present and it shows metal : ligand ratio as 1 : 2 for Cu (II) complex.

On the basis of analytical data, magnetic moment, electronic spectral data, IR, ^{1}H NMR and thermal analysis Cu (II) complexes, the structure of 2'-hydroxychalcone has been assigned with square planar geometry.



Complex No.	R	R$_1$	R$_2$
1	I	H	Cl
2	I	H	Br
3	Br	CH$_3$	Cl

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REFERENCES

1. R. S. Naidu and R. R. Naidu, Inorg. Nucl. Chem., **41**, 1625 (1979).
2. C. M. Devia, N. B. Pappanu and N. B. Debattista, Rev. Microbiol., **29**, 307 (1998).
3. H. Tsuchiya, M. Sato, M. Alkagir, N. Takagi, T. Tanake and M. Linuma, Pharmazie, **49**, 756 (1994).
4. J. R. Dimmock, D. W. Elian, M. A. Beazely and N. M. Kandepu, Curr. Med. Chem., **6**, 1125 (1999).
5. M. L Edwards, D. M. Stemerick and P. S. Sunkara, J. Med. Chem., **33**, 1948 (1990).
6. R. Doshi, P. Kagthara and H. Parekh, Indian J. Chem., **38A**, 348 (1999).
7. Y. Ninomiya, N. Shimma and H. Ishitsuka, Antiviral Res., **13**, 61 (1990).
8. K. Kyogoku, K. Hotayama, S. Yokomori, R. Saiziki, S. Nakane, M. Sasajima, J. Jawadia, M. Ohzeki and I. Tanaka, Chem. Pharm. Bull., **27**, 2943 (1979).
9. S. Fabio, B. Stifania, C. Luca, V. Gabriella, M. Michele and A. Luciano, Eur. J. Med. Chem., **33**, 859 (1998).
10. G. B. Barlin, B. Kotecha and K. H. R Eichman, Aust. J. Chem., **49**, 647 (1996).
11. S. Sung Lim, S. Hoon, J. I. Jung, K. Hyun Shin and S. R. Keum, Chem. Pharm. Bull., **48**, 1786 (2000).
12. K. Syamasunder, Proc. Indian, Acad. Sci., **60**, 259 (1964).
13. K. G. Karamunge, M. E. Sayyed, Archana Y. Vibhute and Y. B. Vibute, J. Indian Chem. Soc., **88**, 443 (2011).
14. V. R. Venkataraman, M. S. Kather and I. Mansoor, J. Indian Chem. Soc., **63**, 925 (1986).
15. M. T. Geasy, Coord. Chem. Rev., **7**, 81 (1971).
16. T. Seetha Rama Rao, K. Laxma Reddy and P. Lingaiah, Proc. Indian Acad. Sci. (Chem. Sci.), **100**, 363 (1988).
17. M. Palaniandavar and C. Natarajan, Aust. J. Chem., **33**, 737 (1980).
18. P. G. More and R. B. Bhalvankar, J. Indian Chem. Soc., **83**, 113 (2006).
19. P. K. Sharma, A. K. Sen and S. N. Dubey, Indian J. Chem., **33A**, 1031 (1994).
20. R. C. Khulbe, Y. K. Bhoon and R. P. Singh, J. Indian Chem. Soc., **50**, 840 (1981).

21. P. R. Athappan and G. Rajagopal, Indian J. Chem. Sec., **33A**, 317 (1997).
22. R. W. Mathew and R. A. Walton, Inorg. Chem., **9**, 143 (1970).
23. S. K. Sengupta, S. K. Sahni and R. N. Kapoor Indian J. Chem., **20A**, 692 (1981).
24. P. P. Hankare, S. R. Naravane, V. M. Bhuse, S. D. Delekar and A. H. Jagtap, Indian J. Chem., **43 A**, 1464 (2004).
25. B. C. Werden, E. Billing and H. B. Gray, Inorg. Chem., **5**, 78 (1966).
26. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Emsterdam, London (1968) p. 209 and 216.
27. A. B. P. Lever, Inorganic Electronic Spectroscopy, Second Edition, Elsevier Emsterdam, London, (1984) pp. 816-820.
28. K. P. Deepa, K. K. Aravindakishan and F. Suhara, Asian J. Chem., **13**, 513 (2001).
29. P. K. Panchal, D. H. Patel and M. N Patel, Synth. React. Inorg. Met.-Org. Chem., **34(7)**, 1223 (2004).

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