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SYNTHESIS AND CHARACTERIZATION OF CHROMIUM (III) COMPLEXES OF P-VANILLIN SEMICARBAZONE AND THIOSEMICARBAZONE

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ABSTRACT: -

Chromium (III) complexes of p-vanillin semicarbazone (L^1) and thiosemicarbazone(L^2) have been synthesized. These complexes were characterized by elemental analysis, molar conductance, magnetic moment, IR, electronic and epr spectral studies. Complexes were found to have Cr ($L_1$and L_2)$_2$ X_3 Composition. Molar conductance indicates that chloro complexes are 1:1 whereas nitrato complexes are 1:2 electrolyte in nature. Both the ligands act as bidentate. On the basis of spectral studies an octahedral geometry has been assigned for all the complexes.

KEYWORDS: Mass IR, Magnetic moment, EPR.

INTRODUCTION:

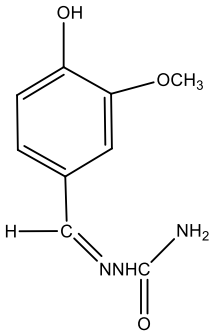
Thiosemicarbazone and semicarbazone act as a chelating agent for metal ion by bonding through sulfur or oxygen [i]. There has been continued interest in ever increasing domain of pharmacological properties of the different thiosemicarbazones and semicarbazones. They have been found to be active against influenza [ii, iii], smallpox [iv] tuberculosis [v-vi], herpes [xi], protozoa [xii], funzi pets [xiii-xv], and a variety of microbes and are also useful - as coccidiostat [xvi-xviii], compounds. Reports on their antiviral [xix-xxiii], anti-tumor [xxiv-xxxii], anti-bacterial [xxxiii], anti-fungal activities and anti- inflammatory and tumor blood flow traces have led to a heightening of interest in the chemistry of these compounds particularly in relation to transition metals. Domagk et.al [vii] reported for the first time the anti-tubercular activities of metal thiosemicarbazone and semicarbazones.

Due to lack of toxicity chromium (III) complexes are used as potential supplement and drugs. Chromium picolinate and chromium nicotinate are the most popular chromium complexes, which are used in the production of drugs [xLiii-xLv].

Chromium (III) is an essential nutrient for mammals, so pharmaceuticals compounds are recommended as a source of this element [xLvi]. In applications of ligands of chromium (III) reported the synthesis of chromium (III) complexes with pvsc (L^1), pvtsc (L^2).

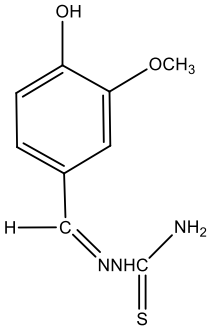
In view of above applications of chromium (III) complexes of semicarbazones and thiosemicarbazones, it is desirable to synthesis and characterize the Cr (III) complexes.

In this paper we report the synthesis and characterization of Cr (III) complexes with p-vanillin semicarbazone (1) and thiosemicarbazone (2).



(p-vanillin semicarbazone) (pvsc-L^1)

(I)



(p-vanillin thiosemicarbazone) (pvtsc-L^2)

(II)

EXPERIMENTAL:

Synthesis of ligands:

Preparation of ligands pvsc L^1, pvtsc L^2 (p-vanillin semicarbazone / thiosemicarbazone):

A hot ethanolic solution (20 mL), solution of p-vanillin (3.04 g) and a hot /aqua ethanolic solution (20 mL) semicarbazide/thiosemicarbazide (1.82 g) were mixed slowly with constant stirring. The white color crystals were precipitated out. It was filtered, washed with 50% ethanol and dried in electric oven at 70°C (yield 65-80 %).

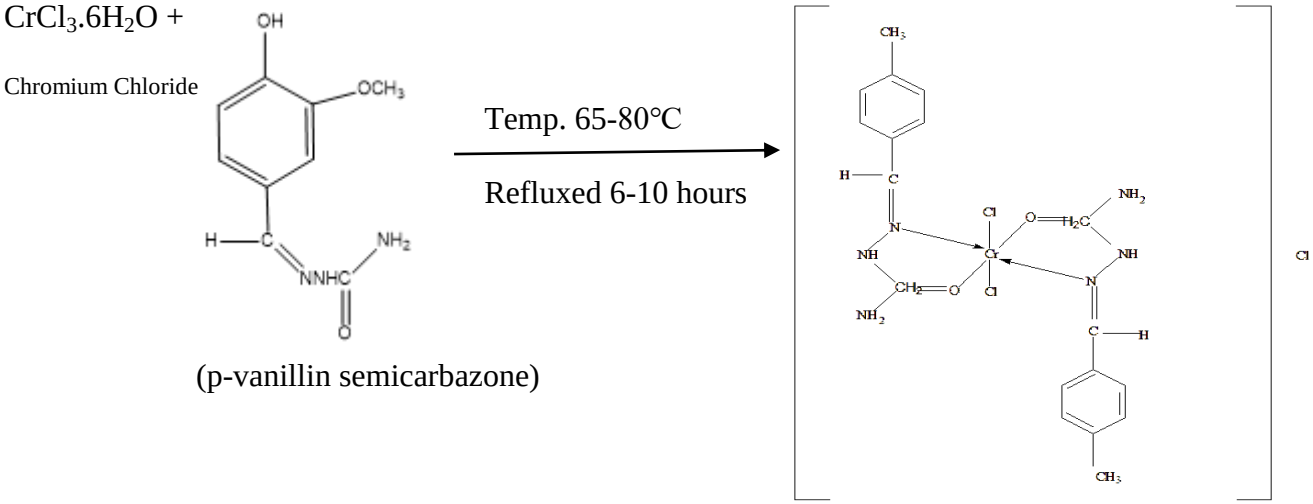
PREPARATION OF COMPLEXES:

A hot ethanolic solution (20 mL) of the chromium salt ($CrCl_3.6H_2O$ or Cr $(NO_3)_3$. $6H_2O$, .001mole) was mixed with a hot ethanolic solution of semicarbazone and thiosemicarbazone of p-vanillin or p-tolualdehyde (.44-g, .002 mole). The mixture was refluxed on a water bath for about 6-10 hours at 65-80°C). After refluxing the mixture was concentrated to half of its original volume. On cooling overnight in a refrigerator, the green to violet-colored crystals of the complexes precipitated out. It was filtered, washed with 50% ethanol and dried under vacuumed over P_4O_{10}.

Physical Measurement: The C, H and N were analyzed in Carlo-Erba 1106 elemental analyzer. Molar Conductance was measured on an ELICO (CM82T) conductivity bridge, Magnetic susceptibility was measured at room temperature, on CAHN-2000 magnetic susceptibility balance using $CuSO_4.5H_2O$ as a calibrant. Infrared Spectra of ligands and complexes were recorded as KBr pellets on a Perkin-Elmer 1310 spectrophotometer. The electronic spectra of complexes were recorded in DMSO, on a Shimadzu UV mimi-1240 spectrophotometer. EPR Spectra of complexes were recorded in JEOL, JES, FE3XG, EPR spectrometer. The spectra were recorded in solid as polycrystalline sample at room temperature E_4-EPR spectrometer using as the g-marker.

RESULTS AND DISCUSSION:

On the basis of elemental analysis all the complexes were found to have the general composition CrL_2X_3 (where L= pvsc (L^1), pvtsc (L^2) and X=Cl^- NO_3^-). The molar conductance of these complexes has been measured in DMSO solution. This indicates that chloro complexes are 1:1 electrolyte in nature, so the complexes may be formulated $[Cr(L)_2Cl_2]$ Cl, whereas the nitrato complexes are 1:2 electrolyte in nature, and may be formulated as $[Cr(L)_2\ NO_3]\ (NO_3)_2$.



(SCHEME-1)

TABLE 1

Complexes	Colour	MP°C	Molar Conductance Ω Mole^2 Cm^{-1}	Yield %	Elemental analysis found and calculated %			
					Cr	C	H	N
[Cr(pvsc)$_2$Cl$_2$] Cl	Green	222	80	60	8.55 (9.07)	35.49 (35.75)	3.64 (3.50)	13.80 (14.00)
[Cr(pvtsc)$_2$Cl$_2$] Cl	Green	218	75	65	8.54 (9.34)	35.49 (35.73)	3.64 (3.39)	15.77 (15.97
[Cr(pvsc)$_2$ NO$_3$] (No$_3$)$_2$	Violet	229	150	71	9.20 (8.33)	33.12 (32.16)	3.60 (2.90)	20.68 (20.54)
[Cr(pvtsc)$_2$ NO$_3$] (No$_3$)$_2$	Brown	232	155	58	8.11 (7.69)	33.76 (32.67)	3.60 (2.97)	19.72 (18.26)

IR SPECTRA:

A Comparative study of the spectra of the ligands and their complexes shows that both the ligands behave as bidentate. A band corresponding to ν (N-H) observed at 3295-3215 cm^{-1} in all the ligands. On complex formation the position of this band remains unchanged. Which indicates that NH group does not coordinate to the metal ion. A new band for ν (C=N) group, observed at 1627-1595 cm^{-1}, the position of this band shifted to a lower frequency 35-45 cm^{-1} in the spectra of the metal complexes which indicate that coordination takes place through azomethine nitrogen. Which is further supported by appearance of a medium intensity band in the range ~439-411 cm^{-1} attributable to ν (M-N). A strong band at 1675/835 cm^{-1} is observed due to ν (C=O/S) spectra of the ligands. On complex formation this band is also shifted to lower frequency in complexes which suggest that coordination takes place

through O/S atom of ν (C=O/S) group respectively. Thus, it has been concluded that all the ligands act as bidentate[40].

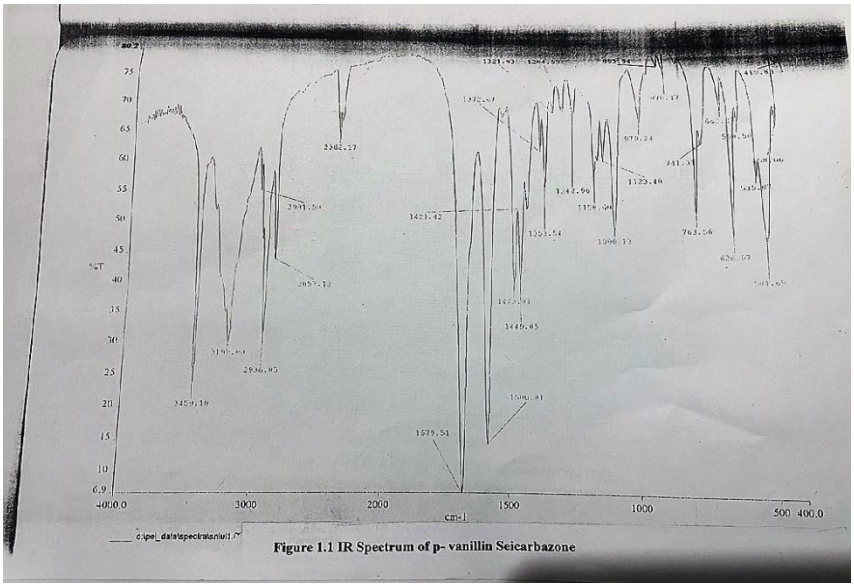


Figure 1.1 IR Spectrum of p- vanillin Seicarbazone

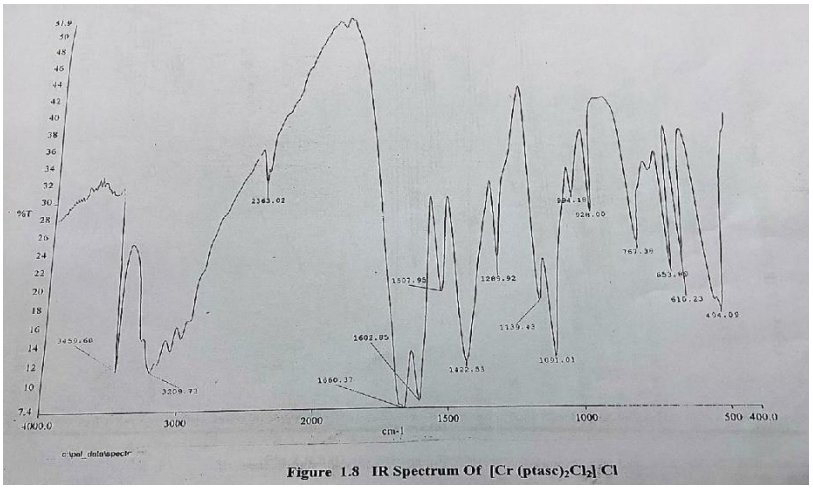
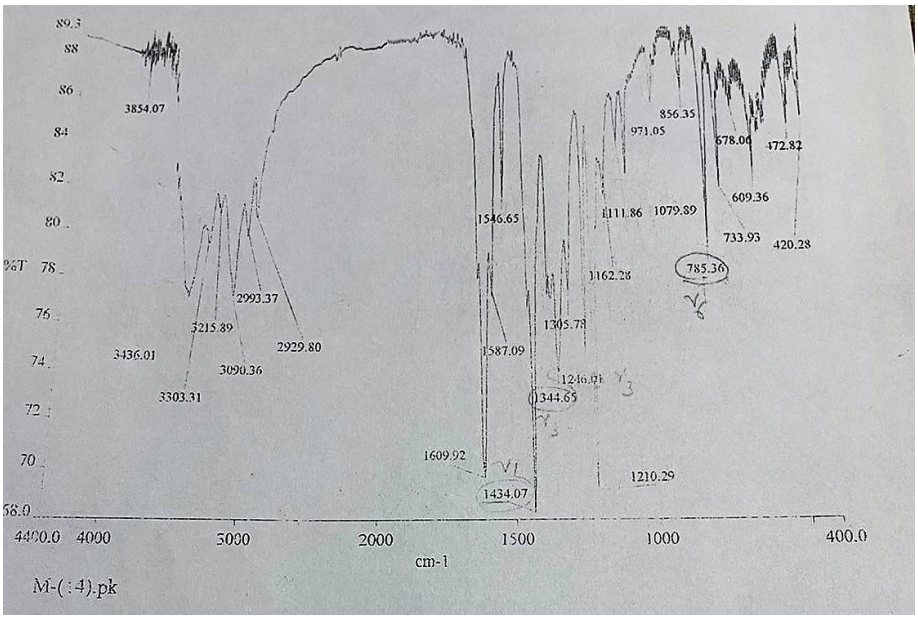
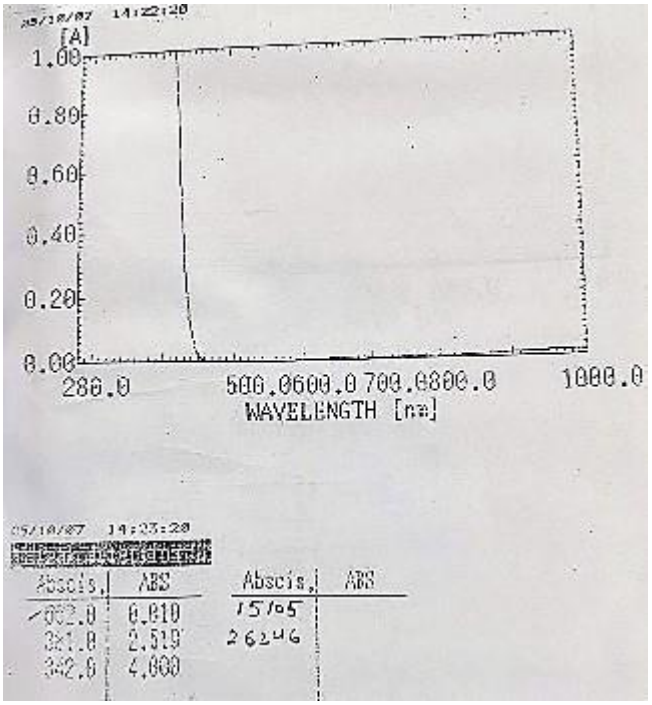


Figure 1.8 IR Spectrum Of $[Cr(ptasc)_2Cl_2]Cl$





BANDS DUE TO ANIONS:

Infrared bands are observed corresponding to both the coordinated and uncoordinated nitrato group. In the present complexes these bands lie in the range of 1546-1429 cm^{-1} (ν_1), 1290-1271 cm^{-1} (ν_5), 1136-1022 cm^{-1} (ν_2), and 838-804 cm^{-1} (ν_6).

The separation between ν_1 and ν_5, is found > 186 which indicates the bidentate nature of the nitrato group. A broad band at near 1392 cm^{-1} corresponding to uncoordinated nitrate.

Magnetic moment of the complexes understudy at room temperature lies in the range of 3.73-3.82 B.M. Corresponding to three unpaired electrons.

TABLE - Ligand field Parameters of Cr (**III**) Complexes:

Complexes	Dq(cm^{-1})	B(cm^{-1})	β	LFSE(K.J.MOL^{-1})	g_{iso}
$[Cr(pvsc)_2cl_2]cl$	1490	580	.632	202	2.00
$[Cr(pvtsc)_2cl_2]cl$	1418	771	.840	203	2.01
$[Cr(pvsc)_2N0_3]$ $(NO_3)_2$	1677	312	.340	240	2.02
$[Cr(pvtsc)_2NO_3]$ $(NO_3)_2$	1689	372	.406	242	2.01

ELECTRONIC SPECTRA:

ELECTRONIC SPECTRA OF CHLORO COMPLEXES:

Electronic spectra of the complexes show bands due to14183-14903cm^{-1}(v_1), 20745-21186cm^{-1}(v_2) corresponding to the spin allowed transition $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$, $^4A_{2g}(F)$-$^4T_{1g}(F)$. The $^4A_{2g}(F)$-$^4T_{1g}(P)$ transition expected, to appear above [47] 30000 cm^{-1}, is usually not observed due to the charge transfer band in the ultra violet region. On the basis of above transition an octahedral geometry may be suggested for the complexes.

Values of the ligand field parameters have been evaluated and present in the table. The thiosemicarbazone complexes have higher Dq values as compared to the semicarbazone complexes. It is due to higher position of the sulfur atom as donor compared to the oxygen atom in the spectrochemical series. Thiosemicarbazide complexes are also known to have larger Dq values as compared to the corresponding semicarbazide complexes [41].

ELECTRONIC SPECTRA OF NITRATO COMPLEXES:

Electronic spectra of the complexes show bands 160778-160890 cm^{-1}(v_1), 20283-21321(v2) cm^1 corresponding to $^4A_{2g}(F)$-$^4T_{2g}(F)$, $^4A_{2g}(F)$-$^4T_{1g}(F)$. The v_3 transition is usually not observed because of charge transfer set in the ultra- violet region. It is important to note that the chloro complexes are green and the nitrato are violet in colour. This differences in colour are associated with marked difference in the electronic spectra as discussed. It has also been observed that the aqueous solution of nitrato complexes, on keeping undergo a colour change from violet -green. It is indicated that the green-coloured species is comparatively more stable and hence, has trans structure; the violet species, thus being cis.

For the same ligand the nitrato complexes show stronger ligand field than the corresponding chloro complexes. The extent of spectral shift from chloro to nitrato complexes is due to the order of approximately 2000 cm^{-1}, which by no means may be attributed to the difference in the ligand field strengths of two anions.

LIGAND FIELD PARAMETERS:

The energy of the $^4A_{2g}$-$^4T_{2g}(F)$ Spin allowed transition gives the value of 10 Dq. The evaluation of B can be made by the use of the following formula[48]

$B=(2V_1^2+V^2{}_2-3V_1V_2)/ (15\ V_2-27V_1)$

Where v_1 and v_2 are the energies of the transitions $^4A_{2g}(F)$-$^4T_{2g}(F)$,$^4A_{2g}(F)$-$^4T_{1g}$(respectively).

The nephelauxetic parameter, B is readily obtained by using the relation: -

β=B(COMPLEX)/B (FREE ION)

Where B free ion=918cm^{-1}. The value lies in the range of 0.31-0.84 indicate that the complexes have appreciable covalent character. The value of **C** Can be calculated by using the relation C=4B.

EPR SPECTRA;

The d^3 ion has relatively long spin -lattice relaxation time and gives narrow ESR absorption line, even at room temperature. In an octahedral symmetry the ground state belongs to the $^4A_{2g}$ irreducible representation and is connected through the spin -orbit coupling to the excited $^4T_{2g}$ states only. For this reason, the g and A term are nearly isotropic, even in highly distorted crystal fields.

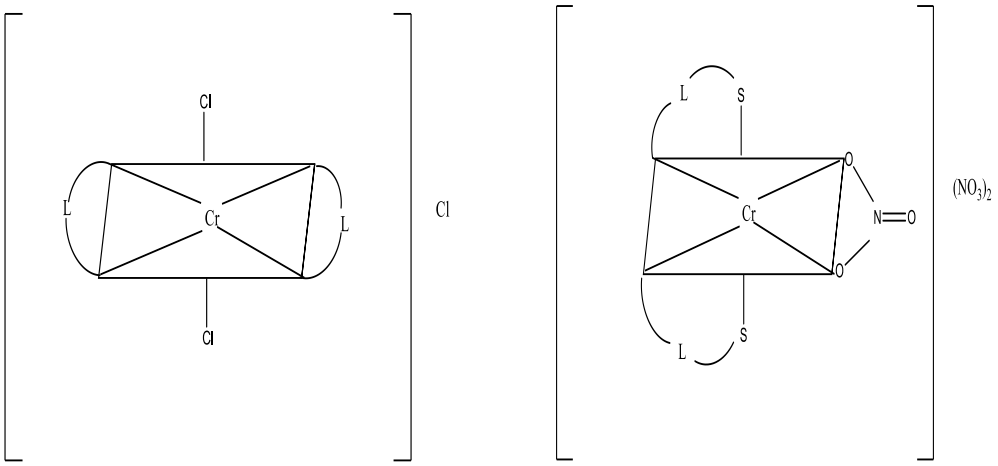
In d^3 ions the symmetry of the crystal field is primarily exhibited through spin- spin terms D and E. In the crystal field theory, the value of g can be calculated by the equation.

$g = 2.0023 - 8\lambda / E(T_{2g})$

Where λ is the spin orbit coupling constant for the metal ion in the complexes.

g values are lies in the range of 2.00-2.01.

On the basis of the aforesaid study such as elemental analysis, molar conductance measurements, magnetic susceptibility, IR, electronic and EPR spectral data, the structures may be proposed for all the complexes.



L= Ligand L= Ligand

CONCLUSION: -

On the basis of elemental analysis, molar conductance, magnetic moment, IR, electronic and EPR a six coordinated octahedral geometry has been assigned. Both the ligands act as bidentate.

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REFERENCES:

I. SinghR.B., Garg B.S. and Singh R.P., Talanta,25,619, (1978).
II. Orlova N.N, Akosevova V. A, Selidovkin D. A, Bogdanova N.S. and Pershin G. N, Russ.Pharm. Toxicol.,23, 384, (1968).
III. Warek S.K.,Teresa and Seczyielskla Jadruiga Acta, Pal.Pharm., 33,17.(1976).
IV. Bauer D.J.,Vincent L.,St.,Kempe C.H. and Downe A.W,Lancet., 2,494,(1963).
V. BauerD.J., Infektionsker,Int.kongr,Infecktionsker Vehandlungsker,4,173,(1968).
VI. Brown R., Fisher R., Blunk J., Berlin k.D, Ramalingam K., Durhan N.N.Proc. Oakla.Acad,Sci.,56,15,(1976).
VII. Domagk G.D., Behnisch R.B, Mietzch F.and Schmidt H., Naturwissens Chaften,

33,315, (1946).

VIII. Kruger T.E., Kroeger H., Nestler H.J.and Scydel J., Infektionskr Uhre Errager, 43, (1975).

IX. Butler K., U.S.Patent No.3, 382,266,7 May (1968).

X. Singh H., kapil R.S., Ind. Jour.App.Chem., 22, 167, (1969).

XI. Addy S.K.and Mitra G.N., Phyto Pathology,56,485, (1966).

XII. Fox O.D., Drew M.G.B., Wilkinson E.J.S.and Beer P.O., Chem. Commun., 319, (2000).

XIII. Johnson C.W., Joyner J.W., and Perry R.P., "Antibiotic Chemotheraphy",2,636, (1952).

XIV. Barret Paul A., Brit I., 143,940(CICo7d) 26Fet 1969, Appl. 25 May, p.8(1965).

XV. Albert A., Jour.Aust. Sci., 30, (1967).

XVI. Loddo B., Minerva Med., 59, 3373, (1968).

XVII. Abram S., Mossmer C.M.,Abram U., Polyhedron,17,131,(1998).

XVIII. More M.S.,Joshi P.G., Mishra Y.k., Khanna P.K., Material today chemistry1., 14:100195,Dec2019.

XIX. Chandra S.,Tyagi M., Journal of the Indian Chemistry Society 85(1): 42-47., Jan2008.

XX. Muleta F., Alansi.T., Eswaramoorthy R., Nat.Sci.Res.,9,33., (2019).

XXI. Annis.I., Kostava,Steel.R.Barry., Catalyst 10(10)1107 (sep2020).

XXII. Franco B., Bacci.Cristina., Vismarra.A., Barilli E., Journal of inorganic Bio chemistry.,203,110888, Oct (2020).

XXIII. Levison W.R.W., Mikelens P.J.J., Antony A.,and Ramakrishanan. T. and Ann N.Y., Aca.Sci., 284,525, (1977).

XXIV. Agarwal K.C., Schenkman J.B., Denk M.M.,Paul D. , Morre E., Collen W.I., Sarlovelli A.C.,Cancer Res., 37,(1977).

XXV. Kumar A., Usha, Chandra S., Synth.React.inorg.Met.Org.Chem., 23,671, (1993).

XXVI. Kang Y., Yang N., Kang S.O., Ko J., Lee C.H.and Lee Y.H., Organomettalic, 16,5522, (1997).

XXVII. Abram S., Maichle-Mossmer C., Abram U., Polyhedron, 17,131, (1998).

XXVIII. West D.X., Swearingen J.K., Valdes-Martinez J., Oretega S.H., El-Sawaf A.K., Van Merries F., Castineiras A., Gracia I., Bermejo E., Polyhedron, 18,2919, (1999).

XXIX. West D.X., Ackerman l.J., Fanwick P.E., Green M.A., John E., Running w.E., Swearingen J.K. and Webb J.M.,Polyhedron, 18,2759,(1999).

XXX. Teoh S.G., Ang S.H., Fun H.K. and Ong C.W., Jour.Org.Chem., 580,17, (1999).

XXXI. Bermejo E.,Carballo R., Castineiras A.,Dominguez R., Maichle-Mossmer C., Strahle J., West D.X., Polyhedron, 18,3695,(1999).

XXXII. Tarasconi P., Capacchis S., PelosiG., Cornia M., Albertini R., Bonati A., Dall Aglio P.P., Lunghi P. and Pinclli S., Bio-Org. Med.Chem., 8,157, (2000).

XXXIII. West D.X.,Carlson C.S., Liberta A.E., Albert J.N. and Daniel C.R., Trans.Met.Chem., 15,383.(1990).

XXXIV. West D.X., Lockwood M.A., and Albert J.N., Spectrochim.Acta,49,1809, (1993).

XXXV. West D.X., Caelson C.S. and Liberta A.E., Trans. Met.chem.,16,53, (1990).

XXXVI. Sharma v.k. and Srivastava., Journal of chemistry., (22 sep2010)

XXXVII. Kumbhar A.S., Pandey S.B., West D.X. and Liberta A.E., Trans.Met. Chem.,16, 276, (1991).

XXXVIII. Ali A., Choudhary D.A. and Nazimuddin M., Polyhedron,3,595, (1984).

XXXIX. S. Zhen-Zh i Z. and Yong X.M., Chem.Pap., 45,373, (1991).
XL. NakamotoK., "Infrared Spectra of inorganic and Coordination Compounds ", Wiley Interascience, NewYork, (1970).
XLI. Campbell M.J. and Crzeskowiak R., Jour. Chem. Soc., A.,396, (1967).
XLII. Donini J.C., Hollenborne B.R., London G., Lever A.B.P and Hempel J.C., Inorg.Chem.,14,455, (1975).
XLIII. Kita E. and Laczna M., Trans.Met.Chem.,26,510, (2001).
XLIV. Kita E.and Szablowicz M., Trans.Met.Chem.28,698, (2003).
XLV. Kita E. and LacunaM., Trans.Met.Chem.,29,762, (2004).
XLVI. Vincent J.B., Polyhedron,20,1, (2001).
XLVII. Lever A.B.P., Inorganic Electronic Spectroscopy, p.275, (Elsevier Publishing Company, Amesterdam) (1968).
XLVIII. Permareddi J.R., Coord. Chem. Rev., 4,73, (1969).

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