



Synthesis and Characterization of New Copper (II) Complexes with mixed ligand of Heterocyclic Dithiocarbamates and 4-picoline,luitidine ,en,(1- 10)phen,pPh₃

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ABSTRACT

New copper (II) complexes containing mixed ligands of the general formula [Cu(4-Hydrpipdte)₂L₂] and [Cu(4-methylpipdte)₂L₂], where (4-Hydrpipdte), (4-methylpipdte)=4-hydroxypiperidinedithiocarbamate , 4-methylpiperidinedithiocarbamate respectively and L= 4-picoline ,luitidine ,en ,(1-10)phen,PPh₃ , have been prepared and characterized by elemental analyses ,conductivity , infrared ,electronic spectra and susceptibility measurements . From the obtained data a square planar geometry was suggested for the bis (dithiocarbamate) copper (II) complex and octahedral geometry for the others has been suggested.

Keyword: Heterocyclic ,Dithiocarbamates, Copper (II) , Complexes , mixed ligand

تحضير وتشخيص معقدات جديدة للنحاس الثنائي مع مزيج من ليكنادات ثنائي

ثايوكاربميت و ٤- بيكولين، ليوتدين، اثلين ثنائي امين، (١-١٠) فينوثرولين

،ثلاثي فنيل فوسفين

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المخلص

تم تحضير معقدات جديدة للنحاس تتضمن ليكنادات مختلطة صيغتها العامة [Cu(4- و [Cu(4-Hydrpipdct)₂L₂

= (4-methylpipdct) و (4-Hydrpipdct), حيث ان methylpipdct)₂L₂

4-methylpiperidinedithiocarbamate و 4-hydroxylpiperidinedithiocarbamate على التوالي و

L = PPh₃, (1-10)phen, en, luitidine, 4-picoline وشخصت المعقدات المحضرة بواسطة تحليل العناصر

وقياسات التوصيلية واطياف الاشعة تحت الحمراء والمرئية وال فوق البنفسجية وقياسات الحساسية المغناطيسية ومن

النتائج تم اقتراح الشكل المربع المستوي للمعقد بس داي ثايوكاربميت نحاس (II) والشكل ثماني السطوح للمعقدات

الاخري.

الكلمات الدالة : معقدات النحاس ، حلقات غير متجانسة ، ثنائي ثايوكاربميت ، ليكنادات مختلطة.



1 .Introduction

Recently, the design and synthesis of coordination complexes have attracted much attention due to their diversity structures as well as potential applications as functional materials and enzymes.[1] Therefore, all kinds of ligands containing nitrogen, oxygen, sulfur or phosphorus are used to synthesize the coordination complexes[2]. Metal dithiocarbamate complexes have been extensively studied. Monomeric, dimeric, polymeric, two-dimensional and three-dimensional structures are all featured amongst these complexes. In copper dithiocarbamate complexes, the copper oxidation states I–III have been accessible[3] because dithiocarbamates have capability to stabilize transition metals in a wide range of oxidation states [4].Some copper (II) complexes with dithiocarbamates have also been reported. Pyrrolidinedithiocarbamate (PDTC) has been shown to exhibit antioxidant, antiviral and anti-inflammatory properties and metal transport in membranes [5].

2. Experimental

Materials and Instrumentation

All reagents and solvents were commercially available high grade materials (Fluka A.G., Riedel-de Haën, BDH) and used as received, Infrared spectra were recorded on a Bruker Tensor 27co. FTIR spectrophotometer in the 400-4000 cm^{-1} range using KBr discs Conductivity measurements were carried out on 10^{-3} M solution of the complexes in DMF using conductivity meter PCM3 Jenway at an 25 $^{\circ}$ temperature. The electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer UV-160 for 10^{-3} M solutions of complexes in DMF as solvent at 25 $^{\circ}$ C using 1 cm quartz cell. Metal content was determined spectrophotometrically using AA670 atomic absorption spectrophotometer. Melting points were recorded on an Electrothermal 9300 apparatus. The magnetic measurements were carried out at 25 $^{\circ}$ C on the solids by Faraday's method using Bruker BM6 instrument.

I.A. Preparation of sodium 4-hydroxyl piperidinedithiocarbamate, Na(4-hpipdct)

4-hydroxyl piperidine (1.01 g, 0.01 mol) was dissolved in 30 ml of water and the resulting solution was cooled in an ice-salt bath. Sodium hydroxide (0.4 g, 0.01 moles) was added to this solution under stirring, followed by carbon disulfide (0.76 g, 0.01 mol). The mixture was stirred for 30 min in the ice-salt bath, then allowed to reach room temperature and stirred for an additional one hour then dried under vacuum. A yellowish white precipitate formed .

I.B. Preparation of 4-methyl piperidinum 4-methylpiperidinedithiocarbamate [S₂CNC₆H₁₂][H₂NC₆H₁₂].

The ligand prepared in different method 4-methylPiperidine (9.91g, 0.1 mol) was dissolved in water (20 mL), and carbon disulfide (7.6g, 0.1mol) was added. The reaction was stirred for 2 h. Chloroform (80 ml) was added and, after vigorous stirring, the aqueous layer discarded. Reduction in solvent volume led to precipitation of an off-white product. Then dried under vacuum.

I.C. Synthesis of complex [Cu (4-hydpipdtc) ₂]

To a solution of sodium 4-hydroxylpiperidinedithiocarbamic (0.5 g, .0025mol) in methanol was added a methanolic solution of CuCl₂.2H₂O (0.203 g, 0.0012 mol) drop wise with constant stirring at room temperature . After 30 min the black precipitate was filtered off and then dried in air.

I.D. Synthesis of complex [Cu (4-hydpipdtc) ₂L₂]

Prepared as in procedure (I.C) using the same weight of metal salt above and after the formation of the precipitate, (0.0025 mol) of(triphenylphosphine) or (4- picoline) or (3,5-lutidine) was added with continuous stirring for 30min, the complex separated out, were filtered, washed with methanol 10 ml then dried under vacuum.

I.E. Synthesis of complex [Cu (4-hydpipdtc) ₂L]

Prepared similarly as in procedure (I.C) using the same weight of metal salt above and after the formation of the precipitate,(0.0012 mol) of (1,10-phenanthroline or ethylenediamine) was added with continuous stirring for 30 min. The complex formed was filtered and washed with methanol 10 ml, then dried under vacuum.

I.F. Synthesis of complex [Cu (4-methylpipdtc) ₂]

Prepared by the same procedure as for I.C using [S₂CNC₆H₁₂][H₂NC₆H₁₂] (1.0 g, 0.003)mol , CuCl₂ 2H₂O (0.254g ,0.0015mol) to formed a black product .

I.G. Synthesis of complex [Cu (4-methylpipdtc) ₂L₂]

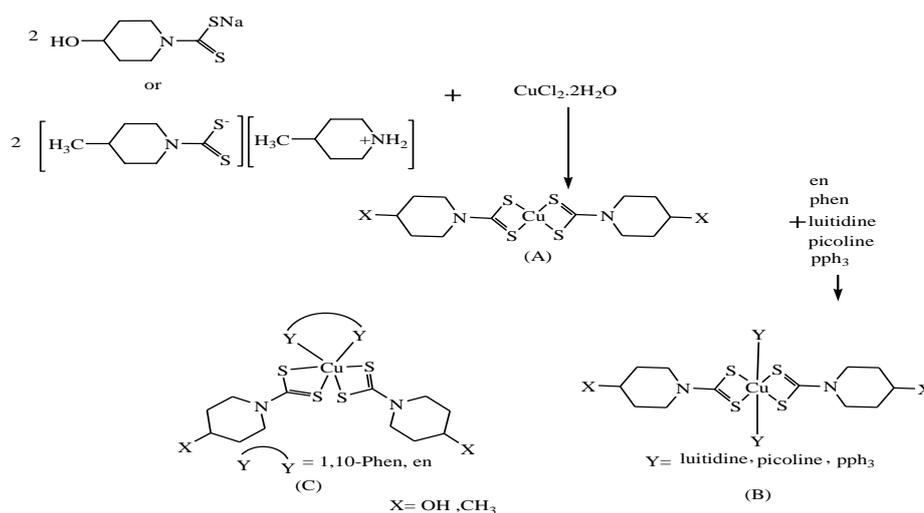
Prepared by the same procedure as for I.F using the same weight of metal salt above after the formation of the precipitate, (0.003 mol) of (triphenylphosphine) or (4- picoline) or (3,5-lutidine) was added with continuous stirring for 30min, the complex separated out, were filtered, washed with methanol 10 ml then dried under vacuum.

I.H. Synthesis of complex [Cu (4-methylpdpdc) ₂L]

Prepared by the same procedure as for **I.F** using the same weight of metal salt above after the formation of the precipitate,(0.0015mol) of (1,10-phenanthroline or ethylenediamine) was added with continuous stirring for 30 min.The complex formed was filtered and washed with methanol 10 ml, then dried under vacuum.

3. Results and discussion

The ligand was prepared by the reaction of carbon disulfide with the secondary amine 4-hydroxypiperidine in the presence of sodium hydroxide and the complexes were prepared by direct addition of the aqueous solution of the copper chloride to the ligand solution in aqueous methanol, using 1:2 (metal: ligand) molar ratio. The base adducts were prepared by adding the base to the prepared bis-complexes in (1:2) or (1:1) molar ratios. **Scheme (1)**.



Scheme (1): Synthesis of ligands, Cu(II) dithiocarbamate complexes, and their Adducts

The composition and analytical data for all complexes are given in Table 1; IR and UV-Visible spectra data are giving in Table 2. The low values of molar conductivities of the complexes (1.0 –14.3 S.cm².mol⁻¹) in DMF solution₂ indicate that all the prepared complexes are non - electrolytes.

Infrared spectra measurements

The most significant bands recorded in the FT-IR spectra of the ligand and the complexes are reported in Table 2. For dithiocarbamate compounds, three main regions of IR spectra are of interest. First, the 1580–1450 cm⁻¹ region, which is primarily associated with the stretching

vibration of C–N group of (N–C) moiety; second the 1060–940 cm^{-1} region, which is associated with m (–CSS) vibrations and a single absorption band in this region suggests a bidentate behavior in $\text{Cu}(\text{dtc})_2$, according to [6] third, the 420–250 cm^{-1} region associated with m (M–S) vibrations [5]. The ligands shows a strong absorption at (1479, 1462) cm^{-1} , which is assigned to the C-N stretching frequency, while the complexes showed an absorption at (1487 -1525), (1496-1506) cm^{-1} respectively, which is assigned to the C=N stretching frequency. In the complexes, if (Cu-S) chelate bonds are formed, then the great contribution of the latter structure will cause the $\nu(\text{C-N})$ bands of the complex to shift to a higher frequency. Compared with the ligand, the $\nu(\text{C-N})$ band of the complex is indeed shifted towards higher frequency by (8-46), (34-44) cm^{-1} respectively. Thus, the 4-hydroxypiperidinedithiocarbamate and 4-methylpiperidinedithiocarbamate ligands coordinate to Copper ions through bidentate sulfur atoms and N-base, PPh_3 . The presence of a single strong band (999 – 1016), (1022-1042) cm^{-1} respectively due to a $\nu(\text{CSS})$ mode in the spectra of the complex is strongly indicative of the bidentate behavior of the dithio ligand in the complexes. [7].

UV-Visible spectroscopy

The UV spectra of the 1,2 ligands showed absorption band at 32187, 31847 cm^{-1} assigned to the transition $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. The complexes 3, 9 show a broad band at 16556, 16447 cm^{-1} which can be attributed to grouping the $[^2B_{1g} \rightarrow ^2A_{1g}]$ and $[^2B_{1g} \rightarrow ^2E_g]$ transitions respectively. The bands at (23584, 32894) (23584, 33557) attributed to charge transfer transitions respectively. [8]. Octahedral copper (II) complexes are expected to show the transitions $[^2B_{1g} \rightarrow ^2A_{1g}]$, $[^2B_{1g} \rightarrow ^2B_{2g}]$, $[^2B_{1g} \rightarrow ^2E_g]$ but bands due to these transitions usually overlap to give often one broad absorption band. [9] Three bands has been observed for other complexes, $\nu(16038-16666)$, $\nu(20833-22935)$, $\nu(31645-34482)$ these band has been assigned to d-d transition and other charge transfer respectively.

Magnetic susceptibility studies

From the Table (1) the 3,9 complexes show values (1.5, 1.77) B.M behavior suggest square planar geometry. [10]. The magnetic moment complex is lower than spin only value could indicate the existence of antiferromagnetic interactions. [7,11]. The other complexes show values (1.76-2.41) B.M due to one electron. Behavior suggests an octahedral geometry. [12,13].

4. Conclusion

From the above discussions the following structures were suggested which indicate a four coordinate geometry around the metal ion with a bidentate coordination ligand through two sulphur atoms Fig. (1) expected have a square planar geometry.

The other six coordinate complexes suggest the coordination via four sulphur atoms of the two 4- substituted piperidinedithiocarbamate ligands and two nitrogen of N-base or two phosphorus atoms of PPh₃ Fig. (2) expected a octahedral geometry.

Table (1): analytical and some physical properties of the prepared ligands and their complexes

Comp. no.	Chemical formula	Color	m.p °C	Yield %	Analysis found (calc.) %					Molar conductivity Ω ⁻¹ .cm ² .mol ⁻¹	μ _{eff}
					C	H	N	S	M		
1.	Na (4-hydpipdtc)	yellowish white	113	90	36.18 (35.89)	5.05 (5.13)	7.03 (6.94)	32.16 (32.25)		----	----
2.	[S ₂ CNC ₆ H ₁₂][H ₂ NC ₆ H ₁₂]	white	115	91	41.58 (41.52)	12.87 (12.68)	13.86 (13.65)	31.68 (30.69)		----	-----
3.	[Cu (4-hydpipdtc)]	Black	266	87	34.66 (34.74)	4.81 (4.63)	6.74 (6.61)	30.81 (30.71)	30.8 (30.7)	4.4	1.50
4.	[Cu (4-hydpipdtc) ₂ (PPh ₃) ₂]	Light green	208	35	38.32 (38.56)	3.73 (3.62)	2.98 (2.78)	13.62 (13.54)	13.62 (13.56)	1.1	2.41
5.	[Cu (4-hydpipdtc) ₂ (en)]	Light black	215	55	35.48 (35.38)	5.91 (5.76)	11.83 (11.74)	27.03 (26.93)	27.03 (26.98)	2.9	1.92
6.	[Cu(4-hydpipdtc) ₂ (4-pic) ₂]	Dark green	187	61	47.88 (47.96)	5.65 (5.42)	9.31 (9.43)	21.28 (21.33)	21.28 (21.39)	1.0	1.76
7.	[Cu (4-hydpipdtc) ₂ (phen)]	Light black	211	51	48.36 (48.43)	4.70 (4.44)	9.40 (9.34)	21.49 (21.33)	21.49 (21.22)	5.3	1.98
8.	[Cu (4-hydpipdtc) ₂ (leuti) ₂]	Light black	180	64	49.56 (49.65)	6.04 (5.88)	8.90 (8.75)	20.33 (19.95)	20.33 (19.93)	14.3	2.33
9.	[Cu (4-methpipdtc) ₂]	black	190	93	40.83 (40.92)	5.83 (5.91)	6.80 (6.91)	31.11 (31.40)	31.11 (31.32)	12.2	1.77
10.	[Cu (4-methpipdtc) ₂ (PPh ₃) ₂]	black	135	55	41.05 (41.17)	4.17 (4.31)	2.99 (3.12)	13.68 (12.88)	13.68 (12.87)	2.0	2.02
11.	[Cu (4-methpipdtc) ₂ (en)]	black	198	57	40.89 (40.78)	6.82 (6.67)	11.93 (11.77)	27.26 (26.77)	27.26 (27.14)	7.2	2.09
12.	[Cu(4-methpipdtc) ₂ (4-pic) ₂]	light green	160	50	52.22 (52.14)	6.36 (6.28)	9.37 (9.17)	21.42 (21.24)	21.42 (21.24)	12.8	2.15
13.	[Cu (4-methpipdtc) ₂ (phen)]	black	175	59	52.75 (52.34)	5.41 (5.59)	9.47 (9.45)	21.64 (21.89)	21.64 (21.44)	12.9	2.32
14.	[Cu (4-methpipdtc) ₂ (leuti) ₂]	black	185	48	53.72 (53.69)	6.71 (6.88)	8.95 (8.64)	20.46 (20.16)	20.46 (20.16)	4.1	2.27

Table (2): IR bands (cm^{-1}) and electronic spectral data of the ligand and prepared complexes.

No.	compound	$\nu(\text{C-S})$	$\nu(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	d-d transition and other absorption cm^{-1}
1.	Na (4-hydpipdte)	949(s)	1479(s)		-	31847 ,33212
2.	$[\text{S}_2\text{CNC}_6\text{H}_{12}][\text{H}_2\text{NC}_6\text{H}_{12}]$	966(s)	1462			32187,35769
3.	$[\text{Cu} (4\text{-hydpipdte})_2]$	1016(w)	1500(m)	-----	482(w)	16156,32894
4.	$[\text{Cu} (4\text{-hydpipdte})_2(\text{PPh}_3)_2]$	999(m)	1525(w)	-----	515(w)	16038,34482
5.	$[\text{Cu} (4\text{-hydpipdte})_2(\text{en})]$	1005(s)	1487(s)	607(w)	484(m)	16666 ,32894
6.	$[\text{Cu}(4\text{-hydpipdte})_2(4\text{-pic})_2]$	1005(w)	1504(m)	558(w)	497(w)	16611,34246
7.	$[\text{Cu} (4\text{-hydpipdte})_2(\text{phen})]$	999(w)	1500(s)	619(w)	485(w)	16124 ,31645
8.	$[\text{Cu} (4\text{-hydpipdte})_2(\text{leuti})_2]$	1005(m)	1506(s)	590(m)	492(w)	16447,32894
9.	$[\text{Cu} (4\text{-methpipdte})_2]$	1024(w)	1504(s)	-----	484(w)	16407,33557
10.	$[\text{Cu} (4\text{-methpipdte})_2(\text{PPh}_3)_2]$	1026(m)	1506(s)	-----	516(w)	16722,36231
11.	$[\text{Cu} (4\text{-methpipdte})_2(\text{en})]$	1042(m)	1496(s)	555(w)	493(w)	16456,34722
12.	$[\text{Cu}(4\text{-methpipdte})_2(4\text{-pic})_2]$	1036(m)	1506(s)	580(w)	494(m)	16233,36764
13.	$[\text{Cu} (4\text{-methpipdte})_2(\text{phen})]$	1024(m)	1502(vs)	576(w)	503(w)	16051,35714
14.	$[\text{Cu} (4\text{-methpipdte})_2(\text{leuti})_2]$	1022(w)	1506(s)	555(w)	494(w)	16356,32679

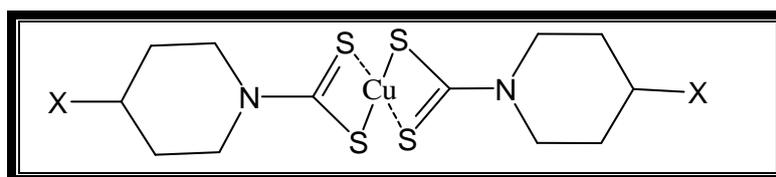
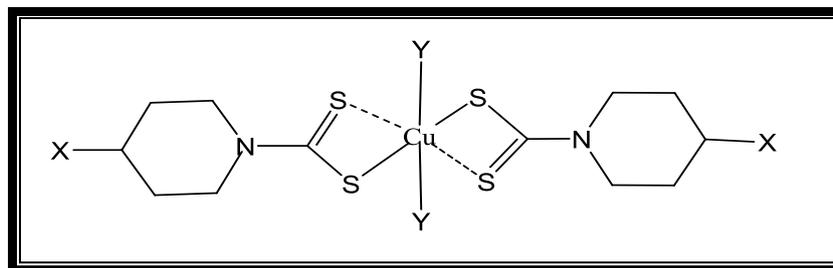
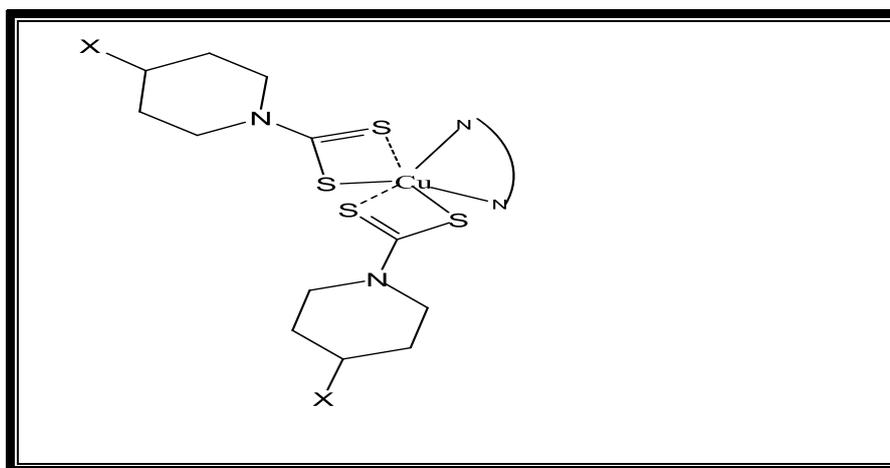


Fig.(1): suggested structure for $[\text{Cu} (4\text{-hydpipdte})_2]$, $\text{X}=\text{OH},\text{CH}_3$



(a)



(b)

Fig.(2): suggested structure for (4-8) [Cu (II) complexes (a) Y=PPh₃, 4- picoline, ,luitidine
(b) en, phen,X= OH,CH₃

REFERENCES

- [1] F.L. Qing, W.J. Hua, L.J. Ming, H. Y. Fang,(2009): *Synthesis and Crystal Structure of a New Cu(II) Dithiocarbamate Complex CuI(prdtc)(phen)*., Chinese J. Struct. Chem, vol.28, No.5, pp.580-584.
- [2] B. Mac´ias, V. M.Villa, E.Chicote, S.M. Velasco, A. Castineiras, and J. Borra´s, (2002): *Copper complexes with dithiocarbamates derived from natural occurring amino acids*. Crystal and molecular structure of[Cu(en)(EtOH)(H₂O)₃][Cu(dtc-pro)₂] ., Polyhedron, vol.21pp. 1899- 1904
- [3] L. F. Hou., Y. Zhong, Y. Mei and J.Fan,(2009): *Bis[N,N-bis(2-hydroxyethyl)dithiocarbamato-k₂S,S']copper(II)*.,Acta.Cryst.vol 65.pp.1664
- [4] Hogarth. G, (2005): *Progress of inorganic chemistry*. Vol.53 p.71.

- [5] M. Sarwar, S. Ahmed, A. sajjad, S. Ali, S. Awan, (2007): *Copper(II) complexes of pyrrolidinedithiocarbamate* .,Transition Metal Chemistry vol. 32 PP.199–203
- [6] K. Nakamoto, (1977): *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley: New York,
- [7] S. P. Sovilj, N. Avramovic, N. Katsaros , (2004): *Syntheses and properties of mixed dinuclear copper(II) complexes with heterocyclic dithiocarbamates and a cyclic octadentate tertiary amine* ., Transition Metal Chemistry.vol.29 pp.737–742
- [8] J. Cookson ,A.L. Emma , P. M.John , J. S. Christopher , L. P .Rowena , R. C. Andrew , G.B. Michael, and D. Paul, (2010): *Metal-directed assembly of large dinuclear copper (II) dithiocarbamateMacrocyclic complexes*. InorganicaChimicaActa No.363 pp. 1195–1203
- [9] A.B. P. Lever, (1984): *Inorganic Electronic Spectroscopy (second edition)*, Elsevier, Amsterdam p.357
- [10] B.J. Hathaway, G. Wilkinson, J.A. McCleverty, R.D. Gillard :(1987) *Comprehensive coordination chemistry in Late Transition Elements* , Pergamon Press, Oxford, vol. 5.p. 656
- [11] A. Golcu, (2006): *Transition metal complexes of propranolol dithiocarbamate: synthesis, characterization, analytical properties and biological activity* . , Transition Metal Chemistry. , vol. 31.pp. 405–412
- [12] A.C. Massey,(1975):*the chemistry of Copper*, silver and Gold, pergamon press, oxford ,pp.20-41
- [13] K. S. Virendra, M. N. Srivastava and H. L. Nigam, (2007): *Coordination and structure of some transition metal piperidiniumpentamethylenedithiocarbamate complexes* ., transition Metal Chemistry .vol 3 No. 1pp. 237-238

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