Asian Journal of Chemistry Vol. 5, No. 3 (1993), 502–506

Complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with *o*-Hydroxyphenylurea

(MISS) Dhiraj SUD and B.S. PANNU*
Department of Chemistry
Punjab Agricultural University
Ludhiana-141 004, India

The metal complexes of *o*-hydroxyphenylurea with composition LMnCl, L_2FeCl, LCo(OH), $LNiCl{\cdot}H_2O$ and LCuCl have been isolated and characterised with elemental analysis, conductance and infrared spectral data. All the complexes are non-ionic and polymers except $LNiCl{\cdot}H_2O$.

INTRODUCTION

Among the ligands containing >C=O as the donor site, *o*-hydroxyphenylurea is especially interesting as it also contains –OH and amine groups. Urea is known to give two types of metal complexes involving donation through carbonyl oxygen or amino nitrogen[1]. Some of the substituted ureas are herbicides while others have cytokinin activity[2]. The phenyl urea derivatives are known to possess anticonvulsive activity[3]. The reaction of trimethylisocyanatosilane with amino alcohols or aminophenols and their silyl ethers have been used to prepare hydroxy alkyl or aryl ureas[4]. The *o*-hydroxyphenylurea cobalt(III) complexes have been reported to be used in photographic materials[5,6]. The hydroxyphenylureas can act as developer in hair dyes[7]. The present investigation describes the preparation and characterization of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of *o*-hydroxyphenylurea.

EXPERIMENTAL

Preparation of *o*-hydroxyphenylurea

Dissolved *o*-aminophenol (0.1 mole) in distilled water (10.0 ml) containing pure HCl (10.0 ml) in 250 ml round-bottom flask and added urea (0.4 mole) in small quantities with continuous shaking. Then added distilled water (30.0 ml), pure HCl (1.0 ml) and glacial acetic acid (1.0 ml). Attached reflux condenser to the flask and refluxed the brownish coloured solution on a slow hot plate for *ca.* 2 hrs. A light brownish compound separated on cooling the solution. Filtered out and crystallized the compound from 50% alcohol twice. Checked its m.pt. 154°C.

Preparation of Mn(II), Co(II), Ni(II) and Cu(II) complexes

Dissolved *o*-hydroxyphenylurea (0.02 mole) in methanol (25.0 ml) and added KOH (0.02 mole) dissolved in methanol (50.0 ml) with continuous stirring. Add this solution to a solution of metal chloride or nitrate (0.01 mole) dissolved in methanol (25.0 ml) with stirring. Transferred the resulting solution to 250 ml round-bottom flask and fitted it with a water condenser. Refluxed the solution on a water bath for about 3 to 4 hrs. Reduced the volume to half by distillation, cooled and filtered out the solid complex formed in a sintered glass crucible G_4 under suction. Washed the compound three times with small quantities of methanol and dried it.

Preparation of Fe(III) complex

The complex of Fe(III) could not be prepared by the method used for other complexes due to greater susceptibility of Fe(III) towards hydrolysis. Dissolved $FeCl_3$ (0.01 mole) in absolute alcohol (30.0 ml) in 250 ml round-bottom flask and added *o*-hydroxyphenylurea (0.03 mole) dissolved in absolute alcohol (50.0 ml). Refluxed the resulting solution for 2 hrs on a water bath. Reduced the volume of the solution to its half by distillation. Added benzene (20.0 ml) and fitted the flask with Dean and Stark apparatus and refluxed the solution for 2 hrs under water condenser on a water bath. Ran off the solvent layer collected in the trap. Reduced the volume of the solution and evaporated it in a vacuum desiccator over fused $CaCl_2$ to get the dry complex.

RESULTS AND DISCUSSION

The analytical data (Table 1) shows that the complexes correspond to the

TABLE 1
ANALYTICAL DATA FOR METAL COMPLEXES OF O-HYDROXYPHENYLUREA

Sl. No.	Empirical formula	Analytical data (%)*			Melting point (°C)
		Metal	Nitrogen	Chlorine	
1.	LMnCl	22.4 (22.75)	11.25 (11.59)	14.9 (14.70)	175
2.	L_2FeCl	14.3 (14.1)	14.15 (14.23)	9.0 (9.02)	184
3.	LCo(OH)	25.70 (25.97)	12.00 (12.33)	—	> 250
4.	$LNiCl\cdot H_2O$	22.3 (22.3)	10.40 (10.63)	13.3 (13.48)	190
5.	LCuCl	25.0 (25.4)	11.30 (11.20)	14.3 (14.2)	> 250

$L = {}^{-}OC_6H_4NHCONH_2$.

*The quantities within parenthesis are the calculated values.

formulae LMnCl, L_2FeCl, LCo(OH), $LNiCl·H_2O$ and LCuCl, where $L = {}^-OC_6H_4NHCONH_2$. All the complexes, xcept $LNiCl·H_2O$, are insoluble in common organic solvents. This reveals the polymeric nature of the complexes except Ni(II) complex. The conductance measurements show their non-ionic character.

In the infrared spectrum of *o*-hydroxyphenylurea there appear four absorption peaks above 3000 cm^{-1}, a medium and broad absorption band at 3515 cm^{-1}, a shoulder at 3460 cm^{-1} and two absorption bands at 3240 cm^{-1} and 3210 cm^{-1}. The first two bands may be assigned to N–H stretching of $-NH_2$ group and third absorption to N–H stretching of –NH– group,[8, 9] the absorption at 3210 cm^{-1} may be due to hydrogen bonded phenolic group[10]. The absorption bands at 1752 cm^{-1} and 1714 cm^{-1} are due to carbonyl group. There appears a strong absorption band at 730 cm^{-1} due to out-of-plane CH fundamental mode. There appears a strong absorption band at 1007 cm^{-1} due to C–N–C stretching mode. The combination band expected at 1737 cm^{-1} due to C–N–C stretching mode at 1007 cm^{-1} and C–H out-of-plane mode at 730 cm^{-1} results in the splitting of the carbonyl stretching band due to Fermi Resonance[11,12]. The absorption at 1622 cm^{-1} is due to δ(N–H) of the primary amide group. The strong absorption at 1458 cm^{-1} may be due to δ(N–H) of secondary amide group mixed with ν(C$\underline{-}$N). The absorption at 1305 cm^{-1} may be due to δ(O–H). The C=O stretching frequency is raised due to the existence of >N- - -H–O hydrogen bonding. The ionic form of *o*-hydroxyphenylurea possesses four sites capable of coordination namely phenoxy oxygen, carbonyl oxygen, primary amide nitrogen and secondary amide nitrogen.

The absorption band corresponding to O–H stretching frequency disappeared on complexation indicating the loss of hydrogen due to metal–oxygen bond formation.

The carbonyl stretching frequency in the case of Mn(II) and Ni(II) complexes is almost the same as that in free ligand while it is lower in the case of Fe(III), Co(II) and Cu(II) complexes (Table 2). These observations indicate that the carbonyl oxygen is coordinated to metal ion in Fe(III), Co(II) and Cu(II) complexes while the carbonyl group is uncoordinated in Mn(II) and Ni(II) complexes.

The vibrational frequencies due to primary amide group are not shifted appreciably in the case of Mn(II) and Ni(II) complexes while the corresponding vibrations are lowered in the case of Cu(II) complex. The absorption due to ν(N–H) of secondary amide group is lowered in the case of Mn(II) and Ni(II) complexes whereas it remained unchanged in the case of Cu(II) complex. These observations suggest that coordination occurs through the nitrogen of the secondary amide group in the Mn(II) and Ni(II) complexes while the coordination is through the nitrogen of the primary amide group in the case of Cu(II) complex. No definite conclusion could be drawn from N–H stretching about the involvement of secondary amide group in coordination in the case of Fe(III) and Co(II) complexes as a broad band appears above 3100 cm^{-1} in their case. There appears

TABLE 2
THE INFRARED ABSORPTION BANDS (cm^{-1}) OF HYDROXYPHENYLUREA AND ITS METAL COMPLEXES IN NUJOL MULL

Compound	ν(N–H) (Primary amide group)	ν(N–H) (Secondary amide group)	ν(C=O)	ν(O–H)	δ(N–H) (Primary amide)
o-hydroxyphenyl-urea	3515 3460	3240	1752 1714	3210	1622
LMnCl	3500 3440	3205	1750 1714	—	1620
L_2FeCl	above 3000 (br)		1660 1640	—	1620
LCo(OH)	above 3000 (br)		1650	—	1620
$LNiCl\cdot H_2O$	3500 3445	3220	1750 1725	—	1625
LCuCl	3420 3330	3240	1660	—	1630

an absorption band at 1460 cm^{-1} in the spectrum of Fe(III) complex which may be due to δ(N–H) of secondary amide group. If the nitrogen of the secondary amide group remains uncoordinated, the N–H bending frequency should be raised due to breaking of hydrogen bonding. This suggests that the nitrogen of the secondary amide group is coordinated to Fe(III).

The appearance of a band at 1640 cm^{-1} in the spectrum of Ni(II) complex indicates the presence of coordinated water. This absorption is due to bending modes of H_2O. The presence of the bridging OH group in the Co(II) complexes is suggested by the sharp absorption band at 1050 cm^{-1} in the spectrum of the complex[8].

The infrared spectrum reveals that *o*-hydroxyphenylurea is coordinated as phenoxy ion to metal ions. The ligand behaves as bidentate through phenoxy oxygen and secondary amide nitrogen in LMnCl and $LNiCl\cdot H_2O$. The coordination sites are phenoxy oxygen and carbonyl oxygen in case of LCo(OH).

In addition to phenoxy oxygen and carbonyl oxygen, the ligand is coordinated through secondary amide nitrogen in L_2FeCl and primary amide nitrogen in LCuCl. The coordination through both carbonyl oxygen and nitrogen of the –NH group in the complexes of phenylurea has already been reported in literature and this supports the present observation[13]. In these complexes *o*-hydroxyphenylurea behaves as a tridentate ligand. The earlier studies on metal complexes of *o*-hydroxyphenylthiourea[14,15] had shown that it behaves as a tridentate ligand. This supports the tridentate nature of *o*-hydroxyphenylurea in the present investigations.

REFERENCES

1. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, p. 209 (1970).
2. M.I. Bruce and J.A. Zwar, *Proc. Roy. Soc., London, Ser. B,* **165** (999), 245 (1966).
3. V. Georgiev and O. Vasileva, *Izv. Inst. Fiziol, Balgar. Akad. Nauk.*, **9**, 105 (1965).
4. V.P. Kozyukov, E.V. Muzovskava and V.F. Mironov, *Zh. Obshch. Khim.***50,** 1425 (1980).
5. A. Adin, J.W. Boettcher and J.C. Flemming, U.S. US4, 294, 912 (Cl. 430–341; G03C1/02) 13 Oct. 1981, Appl. 169, 703, 17 July 1980, 17 pp.; *Chem. Abstr.*, **96,** 113477m (1982).
6. C. Holstead, B.A.J. Clark and M.J. Simons, Brit. U.K. Pat. Appl. GB 2,079, 480 (Cl. G03C100); *Chem. Abstr.,* **96** (21), 190694g (1982).
7. G.R. Hackel, W. Dreher and J. Zschiedrich, Ger DD 208, 298 (Cl. A61 K7/13), 02 May 1984, Appl. 243, 85 08 Sept. 1982; *Chem. Abstr.,* **101** (20), 177207t (1984).
8. E. Spinner, *Spectrochim. Acta.*, **15**, 95 (1959).
9. C.I. Jose, *Spectrochim. Acta.,* **25A**, 111 (1969).
10. A. Vir and B.S. Pannu, *J. Indian Chem. Soc.*, **62**, 322 (1985).
11. C.N.R. Rao, Chemical Application of Infrared Spectroscopy, Acadamic Press, New York, p. 205 (1963).
12. N.B. Colthup, Interpretation of infrared spectra, The American Chemical Society, Washington, p. 87 (1971).
13. P.K. Panda and B.K. Mohapatra, *J. Indian Chem. Soc.,* **57**, 137 (1980).
14. B.B. Mohapatra, B.K. Mohapatra and S. Guru, *Indian J. Chem.,* **16A,** 445 (1978).
15. ______, *J. Indian Chem. Soc.,* **55**, 229 (1978).

(*Received*: 5 September 1991; *Accepted*: 5 September 1992) AJC–475