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SYNTHESIS & CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF Ag(I) METAL CHELATES OF SOME ORGANIC ACIDS WITH ETHYLENEDIAMINE

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Some novel mixed ligand Ag(I) complexes having general formula ML.L', where M = Ag(I), L = deprotonated o-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ) or o-amino-benzoic acid (OABA), L' = ethylenediamine(en) have been synthesized. These complexes have been characterized by physico-chemical studies. The IR spectral data indicate coordination of Ag(I) metal through nitrogen atoms of $-NH_2$ groups of ethylenediamine.

KEYWORDS : Mixed ligand complexes, Ethylenediamine, Ag(I) metal chelate, Infrared spectra.

INTRODUCTION

Silver (I) metal and its compounds find applications in analytical, industrial, pharmaceutical and medicinal fields [1]. Ethylenediamine is an important bidentate cheating ligand. It forms more stable five membered ring with Ag(I) metal ions. It has been well investigated for its coordinating behaviour towards non-transition and transition metals [2-10]. Extending our investigation to synthesize some new mixed ligand complexes of Ag(I) metal chelates of some organic acids with ethylenediamine.

EXPERIMENTAL

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ) or o-nitrobenzoic acid (OABA) and ethylenediamine of AnalaR grade were used as such.

Preparation of Ag(I) metal salts :

Organic acid and sodium hydroxide were taken in 1 : 1 molar ratio in 90% ethanol, and refluxed on hot plate with constant stirring at 80°C for about one hour. The solution was

concentrated and cooled, when the sodium salt of organic acid precipitated out. It was filtered, washed with 90% ethanol and then dried in an electric oven at 100°C.

Again sodium salt of organic acid was dissolved in 90% ethanol. To this an alcoholic solution of $AgNO_3$ were mixed in 1 : 1 molar ratio. The mixture was refluxed on hot plate of magnetic stirrer at 80°C for about half an hour, when coloured precipitate of Ag(I) metal salt of organic acid was obtained. It was filtered, washed with 90% ethanol and then dried in an electric oven at 100°C.

Preparation of Mixed ligand complexes :

To a suspension of Ag(I) metal chelate of organic acid(ML) in 95% ethanol, second ligand (ethylenediamine) was added in 1 : 1 mole ratio. The mixture was refluxed on magnetic hot plate at 80°C with constant stirring for about two hours. The solution was concentrated, cooled to give characteristic coloured precipate. The precipitate was filtered, washed with 95% ethanol and then dried in an electric oven at 100°C.

RESULTS & DISCUSSION

Some physical properties of the ligand(ethylenediamine) and the mixed ligand Ag(I) complexes(ML.L′) obtained are listed in Table 1.

Table 1

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
					H	N	M
Ethylenediamine (en)	Colourless	116.5b	...	...	...	...	
[Ag(ONP).en]	Greenish yellow	>300	6.2	31.10 (31.29)	4.15 (4.24)	13.43 (13.69)	35.01 (35.13
[Ag(DNP).en]	Deep yellow	118m	5.1	27.21 (27.36)	3.05 (3.13)	15.85 (15.96)	30.61 (30.73)
[Ag(TNP).en]	Light brown	112md	5.2	24.19 (24.25)	2.49 (2.52)	17.51 (14.22)	27.01 (27.23)
[Ag(8HQ).en]	Light yellow	298md	6.9	42.25 (42.33)	4.44 (4.49)	13.31 (13.47)	34.22 (34.57)
[Ag(SalA).en]	Yellow	>300	6.6	35.38 (35.43)	4.21 (4.26)	9.02 (9.18)	35.25 (35.37)
[Ag(AcSalA).en]	Cream	262md	5.9	37.85 (37.95)	4.48 (4.60)	7.98 (8.05)	30.79 (30.99)

Ethylenediamine is a colourless liquid, insoluble in cold water but soluble in hot water, ethanol and ether. It is steam volatile. The mixed ligand complexes are of characteristic colours. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc.; but they are sparingly soluble in non-polar solvents, namely, chloroform, *n*-hexane, benzene dioxane etc.

Molar Conductance : Molar conductance of all the compounds were measured in methanol at 33°C at a concentration of 10^{-3} M. The values are given in Table 1. The value of

about 35 - 40 $ohm^{-1}cm^2mole^{-1}$ is characteristic of 1 : 1 electrolyte [11] whereas ideally molar conductance of neutral compound should be zero. However, significantly low values (5.1 - 6.9) of molar conductance of the compounds indicate them to be covalent nature.

Infrared Spectra : Infrared spectra of the ligand (ethylenediamine) and its mixed ligand Ag(I) complexes were recorded in KBr phase between 4000 - 450 cm^{-1} with the help of JASCO-FTIR spectrophotometer model – 5300. Selected absorption bands are listed in Table 2.

Table 2. Pertinent IR data for ligand (ethylenediamine) & its mixed ligand Ag(I) complexes

Compound	υ_{N-H}	δasym N-H	δsym N-H	Rocking NH_2	$\upsilon_{M-O/M-N}$
Ethylenediamine (en)	3377, 3316	1600	1100	810	---
[Ag(ONP).en]	3468	1648, 1610, 1549	1148, 1140	848, 814	654,568, 532, 455
[Ag(DNP).en]	3551, 3375	1604, 1566	1135	837	635, 585, 530, 471
[Ag(TNP).en]	3425	1625, 1590, 1565	1159	820	668, 546, 521
[Ag(TNP).en]	3423	1601	1170, 1114	826	649, 560, 546, 455

In metal amine complexes, the four principle regions of absorptions are nearly 3300, 1600, 1100 and 800 cm^{-1}. These have been assigned to the N-H stretching mode [12] the asymmetric deformation, the symmetric deformation and the NH_2 rocking mode [13] respectively.

In present work, we have found that all the principal regions of absorption 3377 & 3316 cm^{-1} (stretching mode, υ_{N-H}), 1600 cm^{-1}(asymmetric defomation, δ_{N-H}), 1100 cm^{-1} (symmetric defomation, δ_{N-H}) and 800 cm^{-1} (rocking NH_2) are present in ethylenediamine.

The one N-H vibration appears as broad peak in the region 3551-3468 cm^{-1}. The 3377 & 3316 cm^{-1} bands of the ligand(en) are shifted to higher frequency region 3425-3375 cm^{-1} in the complexes. The higher shifting of bands are in conformity with the coordination through the N-H as there has been electron drain from the nitrogen of ethylenediamine to the Ag(I) metal.

Taking into consideration that lower symmetry of cis isomer will give rise to multiplicity in the nearly 1600 cm^{-1} (asym δ_{N-H}) and 1100 cm^{-1} (sym δ_{N-H}), it is observed that these complexes give relatively simple spectra. Two or three bands have been observed between 1648-1549 cm^{-1}. Extra bands are due to presence of - NO_2, -NH_2, -NO of first ligand (*i.e.*, organic acids), very much overlap with other ligand vibration. These complexes also show one or two peaks between 1170-1114 cm^{-1}.

Further the NH_2 rocking at 810 cm^{-1} shifted to higher frequency region 848 - 814 cm^{-1} in all these complexes also indicate coordination of Ag(I) metal through nitrogen atom of - NH_2 group of the ligand.

The band in the region 532 - 455 cm^{-1} in the spectra of all mixed ligand Ag(I) complexes may be assigned to M - O band frequency while medium bands in the region 668 - 546 cm^{-1} assigned to M - N band frequency [14, 15]. The above data confirm the coordination of

oxygen atom of phenolic group and nitrogen atom of –NO/–NO_2/pyridine ring of first ligand, i.e., organic acid to Ag(I) metal ion in all the mixed ligand complexes.

Electronic Spectra : Electronic spectra were recorded on PERKIN ELMER LAMBDA-15 UV-VIS spectrophotometer in paraffin solvent. The bands observed in electronic spectra of the mixed ligand Ag(I) complexes are given in Table 3.

Table 3. Major diffuse reflectance bands(in nm) for mixed ligand Ag(I) complexes with ethylenediamine(en)

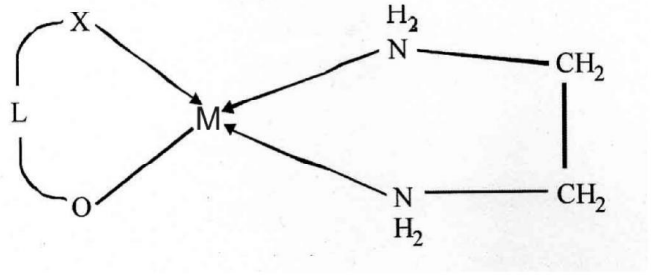
Compound	Diffuse reflectance (in nm)
Ag(DNP).en	353, 250, 236
Ag(TNP).en	390, 351, 339, 240
Ag(8HQ).en	371, 328, 248

Electronic absorption bands of the mixed ligand Ag(I) complexes are observed in the region 236 - 250 nm, which indicate π-π^* transition in the complexes. The mixed ligand complexes also show charge transfer bands in the region 328 - 390 nm.

The shift in position of π-π^* and charge transfer bands of the ligand(en) in the comp-lexes show that there is a π-interaction between metal and ligand orbitals.

STRUCTURE & BONDING

Analytical data lead to the general formula ML.L' for the mixed ligand complexes, where M = Ag(I), L = deprotonated ONP, DNP, TNP, 1N2N, 8HQ or OABA and L' = ethylenediamine(en). Infrared spectral studies suggest the ligand(en) coordinated to Ag(I) metal through nitrogen atoms –NH_2 groups.Above facts suggest the probable structures for these complexes (Fig. 1).



where L = deprotonated ONP, DNP, TNP, 8HQ, 1N2N or OABA; X = O or N

REFERENCES

1. Cotton, F. A. and Wilkinson, G., Adv. Inorg. Chem., Wiley Eastern Pvt. Ltd., p.157, **2nd edn**. (1972).
2. Prakash, D. and Singh, S. P., *J. Ind. Chem. Soc.*, **61**, 471 (1984).
3. Idem., *Polyhedron.*, **7**, 1 (1988).
4. Magyar, B. and Schwarzenbach, G., *Acta Chem. Scand.*, Ser. A., **32**, 943 (1978).
5. Peral, D. P. and Brody, A. R., *Science (Washington D.C.)*, 208, 297 (1980).
6. Timper, U. and Heller, G., *Z. Naturforsch.*, Teil B, **49**, 215 (1994).

7. Kumar, B., Gupta, B. S., Singh, J. P. and Prasad, U., *Acta Cienc. Indica,* **34(1)**,183 (2008).
8. Verma, K., Seema, K. and Chhabra, S., *Int. J. Chem. Sci.*, **6(1)**, 59 (2008).
9. Wankhede, D.S., Hussain, Jadhav, S. N., Wagh, P.B. *et al.*, *Der Chemica Sinica*, **4(5)**, 79 (2013).
10. Krishnan, B.,Vijayanthimala, R. and Nivedha, K.R., *IOSR J. Appl. Chem.*, **8(4)**, 46 (2015).
11. Banerjee, A. K., Layton, A. J. and Nyholm, R. S., *J. Chem. Soc.(A)*, 2536 (1969)
12. Morrison, M. L. and Busch, D. L., *J. Amer. Chem. Soc.*, **82**, 1521 (1960).
13. Chamberlain, M.M. and Bailer, J.C., *Ibid.*, **81**, 6412 (1959).
14. Shyamal, A. and Singhal, O. P., *Trans. Met. Chem.*, **4**, 179 (1995).
15. Condrate, R. A. and Nakamoto, K., *J. Chem. Phys.*, **42**, 2590 (1965).

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