

Coordination Compounds of Cerium(III) Chloride with Oxygen and/or Nitrogen Donor Ligands

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Coordination compounds of cerium(III) chloride with various oxygen and/or nitrogen donor ligands like aliphatic amines, morpholines, piperidines and pyrazole have been prepared and characterised on the basis of elemental analysis infrared and electronic spectral studies. Three types of complexes 2 : 1, 1 : 1 and 1 : 2 are formed.

INTRODUCTION

Coordination compound of CeCl_3 with highly basic ligands have very little been reported perhaps because of their hygroscopicity, insolubility in all organic solvents and ready conversion of Ce(III) to Ce(IV). In continuation of our earlier work¹⁻¹² with these ligands, it was, therefore, thought worth-while to synthesize and study the stoichiometry of these compounds. We report the results on these compounds in this communication.

EXPERIMENTAL

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was obtained from Aldrich Chemical Company, USA and was used as received. The liquid ligands were used after distillation and were stored over KOH pellets. The solid ligands were kept in a desiccator containing KOH for about a week before using. The ligands and solvents were procured as described in our earlier publications¹⁻¹². While absolute ethanol was used as obtained, solvent ether and acetone were dried by usual methods¹³.

Cerium (III) chloride heptahydrate (1 g, 2.68 mmoles) was dissolved in minimum quantity (5 ml) of absolute ethanol in 100 ml round bottom flask and to it was added 50 ml acetone. The ligand (154.56-618.26 mg; 2.68-5.36 mmoles) was dissolved in 5 ml acetone and was added dropwise, with constant stirring to the solution of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ until complete precipitation occurs. Solvent ether was added in excess (50 ml) and the compounds of varying colours were filtered in a G_4 filtration unit. They were dried under vacuum and stored in vacuum sealed vials.

RESULT AND DISCUSSION

All the complexes are hygroscopic insoluble in common organic solvents and decompose in the temperature range 180-210° (Table 1). The insolubility of the complexes in common organic solvents and their non melting nature suggests that they are polymeric.

TABLE 1
ELEMENTAL ANALYSIS, COLOURS AND DECOMPOSITION
TEMP. OF CeCl₃-COMPOUNDS

Sr. No.	Ligand	Colour	Decomp. temp. (°C)	Stoichiometry	M	N	Cl
1.	Ethylene diamine	White	160	1 : 2	39.83 (38.22)	— —	29.04 (29.07)
2.	Diethylene triamine	Light pink	180	1 : 1	40.08 (40.03)	— —	29.58 (30.45)
3.	Triethylene tetramine	Light pink	205	1 : 1	36.22 (39.64)	— —	27.37 (27.11)
4.	Tetraethylene pentamine	Light yellow	268	2 : 1	42.09 (41.09)	— —	31.22 (31.21)
5.	Pentaethylene-hexamine	Pink	220	2 : 1	39.12 (38.60)	— —	28.79 (29.36)
6.	4-Ethyl morpholine	Cream	210	2 : 1	32.68 (32.54)	2.25 (2.79)	24.28 (24.75)
7.	4-Methylmorpholine-N-oxide	Light yellow	140	1 : 1	38.49 (38.48)	3.36 (3.84)	28.85 (29.28)
8.	N-Methylmorpholine	Cream	180	1 : 2	32.05 (31.21)	5.32 (6.24)	24.00 (23.74)
9.	1-Methylpiperidine	Cream	135	1 : 2	32.43 (31.47)	5.63 (6.29)	24.57 (23.44)
10.	2, 6-Dimethyl piperidine	White	200	1 : 2	30.60 (29.60)	6.12 (5.92)	23.37 (22.52)
11.	Pyrazole	White	185-190	1 : 1	43.68 (44.10)	—	34.69 (33.85)
12.	2, 6-Dimethyl-morpholine	Cream	175-180	1 : 2	31.58 (29.35)	5.18 (5.87)	23.54 (22.23)

Cerium was estimated gravimetrically by direct ignition and chlorine analysis was performed volumetrically using Volhard's method. Nitrogen was determined by the standard Kjeldahl's method. IR spectra were recorded as nujol mulls on Hitachi 270-50 spectrophotometer at the Regional sophisticated Instrumentation Centre (RSIC) Punjab University, Chandigarh in the range 4000-250 cm⁻¹. Electronic spectra in the solid state were recorded on a Hitachi 330-UV-visible spectrophotometer at the Department of Chemistry, Punjab University, Chandigarh in the range 2000-200 nm. Elemental analysis data are recorded in the Table 1. The stoichiometries of the compounds formed which have been indicated by elemental analysis and other physical studies were also confirmed by infrared spectra.

In all the compounds containing NH grouping, the shape and position of the band due to NH stretching and bending modes is quite informative in determining the coordination of these ligands¹⁴. In free ligands this stretch appears as a broad band at about 3400 cm^{-1} . Upon coordination this band shifts to lower wave numbers at around 3300 cm^{-1} . The position of NH bonding mode also supports this argument. The band due to this mode appears at about 1650 cm^{-1} in the free ligand and at around 1630 cm^{-1} in the compounds¹⁴. The broadness of these two bands has been attributed to the various modes of association (H-bonding) prevailing in the free ligands and the compounds¹⁴.

The morpholines contain both N and O in the six-membered ring. They can form complexes both in chair as well as in the boat form. The mode of coordination of these ligands can be inferred from shifts in the CH stretch of the alkyl groups attached to the N of the ring and the COC stretch. In the present case the CH stretch which appears in the free ligand at 2850 cm^{-1} , is not located in the IR spectra of the complexes. It probably mixes with the other CH absorptions by shifting to higher wave numbers¹⁵. The COC stretch that was observed as a group of three sharp peaks in the 1100–1000 cm^{-1} region was replaced by two split rounded peaks upon complexation. It is thus indicated that the morpholines are coordinated in a bidentate fashion coordinating via both N and O atoms. The compound with 4-ethylmorpholine should definitely contain this ligand in a bridging bidentate manner in the light of its metal ligand stoichiometry of 2 : 1.

The strong hydrogen bonded NH stretching mode appearing in the region 3200–2850 cm^{-1} was replaced by a much less broader band at 3250 cm^{-1} in the pyrazole complex¹⁴. The coordination of this ligand which is indicated by this change was supported by a shift in the NH bending vibration in the free ligand from 1650 cm^{-1} to 1620 cm^{-1} in the compound. A further indication about the coordination of this ligand comes from C=N stretch. This mode¹⁴ which appears at 1540 cm^{-1} in the free ligand, shifts upon coordination at 1500 cm^{-1} .

The electronic spectra of these compounds were recorded as solids in the range 2000–200 nm. There were no absorptions in the visible region, which supports the established beliefs of the earlier workers. A strong charge transfer band, sometimes split, was recorded in the region 300–350 nm¹⁶.

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