Thermochimica Acta, 200 (1992) 355–360
Elsevier Science Publishers B.V., Amsterdam

Preparation and characterisation of main group and transition metal compounds containing ligands with N- and O-donor atoms

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(Received 16 August 1991)

1. INTRODUCTION

Organic ligands containing N- and O-donor atoms have been found to combine readily with salts of the transition and main group elements; therefore, they form the basis of the work submitted to this journal and reviewed in this paper. Several areas of research were investigated: firstly, many new compounds of the pyridines, pyrazines, and mono- and dicarboxylic acids were prepared; secondly, structural characterisation of the compounds was undertaken using spectral and magnetic studies; thirdly, the stability of the compounds was investigated using thermal analysis to reveal decomposition patterns; and fourthly, electrical conductivity measurements were obtained for selected compounds in order to ascertain their electrical behaviour.

2. PREPARATION OF THE COMPOUNDS

The compounds were generally prepared using stoichiometric amounts of the metal salt and ligand in either aqueous or non-aqueous solvents such as ethanol. Purification of the compounds usually involved washing with warm water or warm ethanol.

3. ANALYTICAL, THERMAL AND ELECTRICAL MEASUREMENTS

The stoichiometry of the compounds was determined using a Carlo Erba elemental analyser for carbon, nitrogen and hydrogen analyses.

The metal analysis was performed using a Perkin-Elmer 373 atomic absorption spectrophotometer, and volumetric and gravimetric analyses.

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0040-6031/92/$05.00

The halide content was determined by argentometric titration and by gravimetric analysis.

The stereochemistry of the compounds was obtained from infrared spectra using KBr discs, 4000–600 cm^{-1}, and polyethylene discs, 600–200 cm^{-1}, on a Perkin-Elmer infrared spectrophotometer, Model 598. The electronic absorption spectra were obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra and the magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

The thermal analysis studies were carried out on Stanton Redcroft Models STA 1500 and STA 781 thermobalances in static air.

Electrical data, involving measurement of the current–voltage characteristics at room temperature and the temperature dependence of the conductivity, were obtained using discs formed from the compressed compounds. The methods are described in detail in the papers.

4. STRUCTURAL CHARACTERISATION

The mono-metallic compounds isolated from solution had mainly stoichiometries ML_2X_2, MLX_2, $M'L_2$ and $M'L$, where M is a transition element or a main group element, M′ is a transition element, X is a halogen and L is an organic ligand. Some of the compounds were isolated from solution in the hydrated form. Mixed metal compounds were also prepared with stoichiometries $[Si(acac)_3]FeCl_4$ and $[Si(acac)_3]MCl_3$, where M is cobalt, copper and zinc, and acac is 2,4-pentanedione [1]. Novel metal complexes were prepared by the reaction of mono- and di-acetylenes with some transition metals [2,3].

The stereochemistry of the compounds was obtained using magnetic measurements, and from electronic and far-infrared spectra. In general, the majority of compounds had octahedral or tetrahedral structures. The compound dichloro(2-methylquinoxaline-N^4)mercury(II) was found to have an unusual polymeric octahedral structure with bridging chlorine atoms between parallel dimeric units [4]; mercury compounds of coordination numbers two and four are much more common. The mode of bonding in the compounds was obtained using near-infrared spectra, particularly the $\nu(CO)$, $\nu(NH_2)$ and ring vibrations [5–7].

5. THERMAL ANALYSIS

Thermal analysis studies have involved the use of thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The decomposition pathway of numerous compounds was examined using TG and DTA. In many instances, intermediate compounds were observed and isolated [7–13]. The final stage of the decomposition process produced either the metal halide or metal oxide. TG and DTA observations of the decomposition processes for the mono- and dicarboxylic acid transition metal compounds almost invariably produced no intermediate compounds.

In some compounds the fusion enthalpy and heat of hydration values were obtained from DTA and DSC [2,14,15]. The difference between coordinated water and water of crystallisation was examined using infrared spectroscopy in conjunction with thermal analysis. Infrared studies of pyridine carboxylic acids with some transition metals showed that coordinated and uncoordinated water are present in the same compound. Unexpectedly, thermal analysis showed that both types of water were driven off simultaneously during decomposition [16,17]. Studies of the compounds which comprised mainly of transition metals with substituted pyridines are reported in refs. 7,10,13,16–21; those of compounds derived from mono- and dicarboxylic acids are reported in refs. 22–31.

6. ELECTRICAL STUDIES

A range of metal complexes of differing stereochemistry were prepared, with emphasis on obtaining polymeric systems; some mixed metal complexes were also prepared. Both main group metals and transition metals were used to obtain the complexes. The ligands chosen were those with N- and O-donor atoms. To study the effect of varying the substituents in a ring system on the electrical conductivity, the pyridine [7,12,32,33] and pyrazine [4,8,9,34–36] rings were chosen as the basic unit. The effect of a multi-ring system on the electrical conductivity was also investigated. The purpose of the work was to produce materials which have semiconductor properties and possible device applications.

Thermal analysis studies were useful in assessing the stability of the complexes and in certain instances good correlation was observed for temperatures from both the electrical measurements and the thermal analysis [8]. The effects observed in these compounds in the electrical measurements were ohmic behaviour [34], space charge limited conduction [4,9,34,37,38], polarisation [8], hysteresis [1,4,32,33,39] and current saturation [4,8]. Problems were encountered when trying to obtain electrical measurements for the compound tris(1-phenyl-3-butanedionato) europium(III). Thermal decomposition studies revealed that this compound undergoes hydrolysis [40]. In the compounds formed between some transition elements and pyrazine-2,3-dicarboxylic acid, a current component opposing the applied voltage was observed and is considered to be due to the optical release of electrons [34]. For dichloro[6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline]nickel, ohmic behaviour was observed at room temperature. On reversal of the polarity, an increase in conductivity was produced. However, on returning to the original polarity, the conductivity was found to be higher than the original measurement. This suggested that the compound had undergone some structural change. A novel application of infrared attenuated reflectance spectroscopy was used to provide evidence for molecular distortion of the ligand when introduced into the applied electric field and thus the observed electrical characteristics of the compound were explained [39]. Current saturation and hysteresis were observed for the compound formed between cadmium bromide and 2-methyl quinoxaline. Space charge effects were observed for the chloro and bromo compounds of 2-methylquinoxaline with zinc and mercury, and were also seen for the chloro complex of cadmium with 2-methylquinoxaline. Thermal decomposition studies showed that the cadmium and zinc compounds decomposed with loss of organic ligand and halogen to form the metal oxide. The mercury compounds decomposed rapidly with complete evolution of the sample [4]. In most cases where substituted pyridines were used, the pyridine ring was fused or linked to benzenoid moieties and ohmic and non-ohmic behaviour was observed; however, in the case of 2,3-cyclododecenopyridine, the pyridine ring was fused to an alicyclic system. A linear correlation was observed between ln σ_0 and ΔE where these quantities are defined by

$$\sigma = \sigma_0 \exp(-\Delta E/2kT)$$

for temperature dependence conductivity. The correlation was believed to be either associated with tunnelling of electrons between intermolecular barriers, or due to carrier tunnelling injection from the electrodes through a surface barrier [12]. These characteristics were also observed in the complexes of the vinylpyridines with cobalt [20,21]. The complexes of 3-(3-pyridyl)acrylic acid with some transition metals in which the C=C group of the 3-(3-pyridyl)acrylic acid is not involved in complexation, showed hysteresis in their electrical behaviour; this was attributed to the current arising from dipolar orientation. The unusual hysteresis produced was considered to be due to the olefinic bond [32]. A similar phenomenon was observed for complexes of acrylamide with some transition metals [41].

Electrical conductivity studies on metal complexes of porphyrin and phthalocyanine ring systems [37,38] have revealed conductivities much lower than those observed for the quinoxaline compounds [8]. This was a surprising observation because it was expected that the highly conjugated electron system in the porphyrins would give higher conductivities. Further studies were carried out on the metalloporphyrin ring system by reacting the planar ring system with pyrazine and a substituted pyrazine. Infrared studies using the pyrazine ring vibration around 1570 cm^{-1} showed that it was strongly influenced by whether the pyrazine molecule acts as a terminal ligand or forms a bridged system with the metalloporphyrin. In the case of the pyrazine acting as a terminal ligand, there was a strong contribution to the absorption band. However, in the case of the pyrazine acting as a bridging ligand, the contribution to the absorption band was negligible. It was concluded that the substituted pyrazine molecule acted as a terminal ligand, while the pyrazine acted as a bridging ligand between metalloporphyrin molecules. Further support for the substituted pyrazine acting as a terminal ligand was obtained from X-ray data. Electrical studies on both the bridged and non-bridged systems showed that most carrier transfer takes place in the layers of the metalloporphyrin, not through the attached pyrazines [42,43]. Electrical studies on silicon/transition metal compounds revealed that the compound [Si(acac)$_3$]ZnCl$_3$ has a conductivity that is suitable for device applications [1]. Of all the compounds studied, those which contained quinoxaline were found to have the highest conductivities.

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