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Dimethylplatinum (II) complexes with isocyanocoumarin ligands: the crystal structure of *cis*-dimethylbis-(7-diethylamino-3-isocyanocoumarin)platinum(II)

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Abstract

Platinum complexes that contain isocyanocourmarin ligands have been prepared. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $[PtPh_2(SMe_2)_2]$ react with ligands L, (L = 7-diethylamino-3-isocyanocoumarin, Idc; 7-isocyano-4-methylcoumarin, Mic; 7-isocyano-4-trifluoromethylcoumarin, Tic; 3-chloro-4-methyl-7-isocyanocoumarin, Cmic), to give PtR_2L_2, monomers in high yield. The NMR and IR spectra of these complexes are consistent with *cis* stereochemistry. The UV–Vis absorption spectra of the complexes show bands assigned to ligand-centered transitions. Excitation into the absorption bands of the Idc complexes gives emission at room temperature in methylene chloride solution. The oxidative addition reaction of two of these complexes with methyl iodide has been studied. Platinum (IV) species with *fac* geometry have been isolated and characterized. *Cis*-dimethylbis-(7-diethylamino-3-isocyanocoumarin)platinum(II) was characterized by X-ray diffraction.

Keywords: Platinum; Oxidative addition; Photochemistry; Isocyanide; Coumarin

1. Introduction

Square-planar platinum (II) complexes with metal-to-ligand charge transfer (MLCT) excited states have been the subject of considerable interest due to their interesting photophysical properties, their potential applications as light emitting diodes, and as devices for solar energy conversion and hydrogen production [1]. The vast majority of these studies have focused on Pt(II) complexes of polypyridyl-type ligands. We thought it would be interesting to examine other Pt(II) complexes also likely to exhibit MLCT excited states. Therefore, in this work we describe the synthesis and characterization of a series of $R_2Pt(CNR)_2$ (R = Me, Ph) complexes where CNR is an isocyanocoumarin ligand (7-diethylamino-3-isocyanocoumarin, Idc; 7-isocyano-4-methylcoumarin, Mic; 7-isocyano-4-trifluoromethylcoumarin, Tic; 3-chloro-4-methyl-7-isocyanocoumarin, Cmic). The preparation of three of the isocyanocoumarin ligands and the $Mo(CO)_4L_2$ complexes of the ligands was recently reported [2]. The molybdenum complexes displayed intense visible absorption and emission bands that were assigned to MLCT transitions. The assignment was, in part, based on the similarities between the isocyanocoumarin complexes and analogous $Mo(pp)(CO)_4$ complexes (pp = polypyridyl) which have very well characterized emissive MLCT excited states [3]. It seems reasonable that MLCT excited states should also be observed for Pt–isocyanocoumarin complexes. We also report the preparation of a new isocyanocoumarin ligand, Idc, which differs from the other isocyano-

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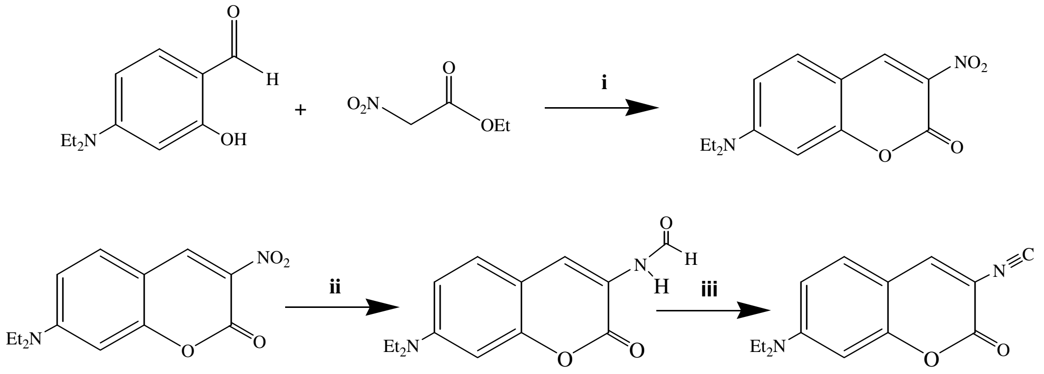

Scheme 1. (i) Reflux in toluene with piperidine. (ii) Reflux with Sn in toluene/formic acid. (iii) Stir with $POCL_3$/NEt_3 in CH_2Cl_2.

coumarin ligands in that it contains an intramolecular charge transfer (ICT) chromophore which generates intense visible absorption and emission bands. There is considerable evidence in the literature that platinum complexes with isocyanide ligands should be stable and display interesting properties. Recent reports on Pt(II)–isocyanide complexes have explored their liquid crystal properties [4], their use as probes for important intermediates in platinum catalyzed reactions [5], and their use as vapochromic sensors [6]. Coumarins and their derivatives [7] are of interest in natural products chemistry [8], have been shown to bond with DNA [9], and have exciting photochemical and photophysical properties of their own [10].

2. Preparation and characterization of 7-diethylamino-3-isocyanocoumarin (Idc)

Idc is easily prepared in the three steps shown in Scheme 1. Idc was fully characterized by elemental analysis, and by NMR, IR, UV–Vis, and emission spectroscopies. The absorbance spectrum (Fig. 1) in CH_2Cl_2 solution is dominated by an intense band at 420 nm. Also shown in Fig. 1 is the intense emission centered at 490 nm generated by excitation into the absorption band. Both the absorption and emission bands are consistent with what has been observed for other 7-aminocoumarin compounds [2]. The emissive excited state can be represented by the resonance structure on the right shown below (Fig. 2) where charge has been transferred from the amine to the unsaturated lactone ring.

3. Synthesis and characterization of the $PtR_2(CNR)_2$ complexes, R = Me or Ph

$Pt(CH_3)_2(CNR)_2$ complexes were readily prepared from $[Pt(CH_3)_2(\mu\text{-}SMe_2)]_2$ and $PtPh_2(CNR)_2$ complexes were prepared from $PtPh_2$ $(SMe_2)_2$ by displacement of the sulfide ligand with an isocyanocoumarin ligand (Chart 1) by mixing the appropriate ligand with the metal complex. Complexes were isolated in high yield as light yellow (Mic, Tic, Cmic complexes) or yellow-orange (Idc complexes) powders (Chart 1 and Reactions (1) and (2)).

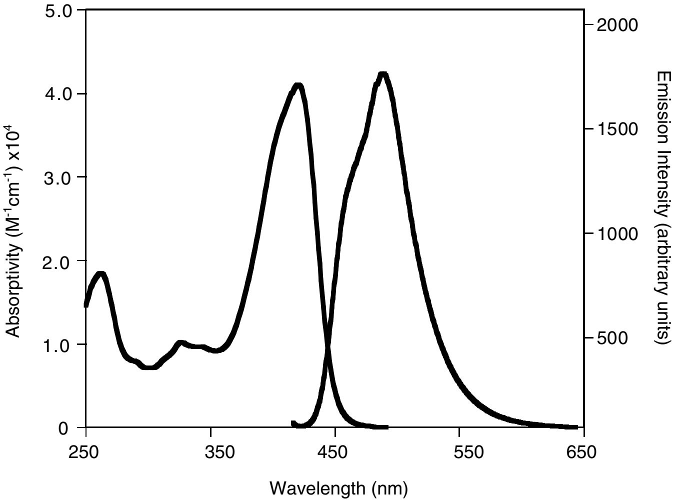

Fig. 1. Absorption and emission spectra of Idc in methylene chloride solution.