

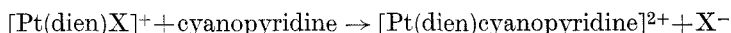
SHORT COMMUNICATIONS

CYANOPYRIDINE COMPLEXES OF PLATINUM(II)

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[Manuscript received January 25, 1971]

Halogenodiethylenetriamineplatinum(II) halides react with a variety of nucleophiles, whereby the halogeno ligand in the complex is replaced. For a given complex, the facility of replacement depends on the nature of the nucleophile. The reactivity of the chloro complex towards acetonitrile in 58% aqueous ethanol (k_2 1.55×10^{-5} dm³ mol⁻¹ s⁻¹; ΔH^\ddagger 71 kJ mol⁻¹; ΔS^\ddagger -98 J K⁻¹ mol⁻¹)¹ is about one-hundredth of that towards pyridine under comparable conditions. This indicates that the nucleophilic power of the pyridine nitrogen is greater than that of the cyano nitrogen. Cyanopyridines are in this respect of particular interest, since they contain both types of nucleophilic site in the same molecule. Therefore the nature of the product obtained from the reaction



(dien = diethylenetriamine) will depend on the interplay of nucleophilic power on the one hand and steric hindrance on the other.

In this work, we have prepared and characterized two cyanopyridinediethylenetriamineplatinum(II) complexes. The infrared absorption peak at 2270 cm⁻¹, assignable to the C≡N stretching vibration in the free ligand, was found to be shifted to lower wave numbers for the 2-cyanopyridine isomer, but to remain unchanged for the 3-cyanopyridine complex. Attempts to isolate the 4-cyanopyridine isomer in the pure state have not been successful, as a highly hygroscopic semi-solid was obtained.

Provided that steric factors are not prohibitive, cyanopyridines will preferentially coordinate through the pyridine nitrogen, which has a greater nucleophilic power than the cyano nitrogen, and this is expected to be the case with 3-cyanopyridine. For 2-cyanopyridine, however, steric hindrance is considerable, but a less hindered pathway for reaction might be possible by making use of the nitrogen atom on the cyano group as a donating atom. These considerations are confirmed by infrared spectroscopic evidence, where coordination through the cyano nitrogen has the effect of reducing the bond-order of the C≡N triple bond.

Experimental

2-Cyanopyridinediethylenetriamineplatinum(II) bromide was prepared by adding a solution of 2-cyanopyridine (0.1 g) in water (5 cm³) to bromo(diethylenetriamine)platinum(II) bromide² (0.1 g) dissolved in water (10 cm³). The mixture was allowed to stand overnight at room tem-

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¹ Chan, S. C., and Tong, S. B., unpublished data.

² Mann, F. G., *J. chem. Soc.*, 1934, 466.

perature and then evaporated under reduced pressure to dryness. The excess 2-cyanopyridine was removed by washing the *solid* several times with ligroin and then with ether (Found: C, 20.7; H, 3.3; Br, 29.0; N, 13.0. $[\text{Pt}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{C}_6\text{H}_4\text{N}_2)]\text{Br}_2$ requires C, 21.4; H, 3.1; Br, 28.5; N, 12.5%).

3-Cyanopyridinediethylenetriamineplatinum(II) bromide was prepared by a similar method using a solution of 3-cyanopyridine in water, except that in this case the *product* was washed with ether only (Found: C, 21.0; H, 3.6; Br, 27.6; N, 12.5. $[\text{Pt}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{C}_6\text{H}_4\text{N}_2)]\text{Br}_2$ requires C, 21.4; H, 3.1; Br, 28.5; N, 12.5%).

Infrared measurements were made with a Perkin-Elmer 337 spectrometer on the solid complex (Nujol) with KBr plates.

Acknowledgment

We thank the Committee on Higher Degree and Research Grants of the University of Hong Kong for financial assistance.