

MULTINUCLEAR VARIABLE TEMPERATURE NMR STUDIES ON CYANIDE, WATER AND HYDROXYL GROUP SCRAMBLING ON HALOGENATION OF $K_2[Pt(CN)_4]$ AND RELATED REACTIONS

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ABSTRACT: ^{195}Pt and 1H NMR has been used to show that addition of chlorine and bromine to $[Pt(CN)_4]^{2-}$ in presence of perchloric acid in water results in cyanide and water scrambling with formation of eleven complexes of the type $[Pt(CN)_{4-n}Cl(H_2O)_{n+1}]^{(n-1)+}$ ($n = 0, 1, 2, 3, 4$). Addition of NBu_4OH to this solution gives $(NBu_4)_2[Pt(CN)_4Cl(OH)]$. NMR measurements in acetone also show cyanide and hydroxyl group scrambling with formation of complexes of the type $[Pt(CN)_{4-n}Cl(OH)_{n+1}]^{2-}$, ($n = 0, 1, 2, 3, 4$).

KEY WORDS: Multinuclear NMR, Scrambling, Halogenation.

INTRODUCTION

Halogen scrambling is wide spread when preparing complexes which contain mixed halogens via oxidative-addition reactions [1,2]. It was claimed on the basis of visible spectroscopic studies that oxidative reaction of $[Pt(CN)_4]^{2-}$ with bromine in presence of perchloric acid in $pH < 3$ results initially in formation of *trans*- $[Pt(CN)_4Br_2]^{2-}$ [3,4]. Vulik et al. have prepared *trans*- $[Pt(CN)_4Br(OH_2)]^-$ with a similar procedure in $pH < 7$ [5]. Drougge and Elding have studied oxidative addition reactions of $[Pt(CN)_4]^{2-}$ with Cl_2 in $pH < 7$ which obtained *trans*- $[Pt(CN)_4 - Cl(OH_2)]^-$ [6,7].

EXPERIMENTAL

^{195}Pt and 1H NMR spectra were recorded on JEOL FX-90Q Spectrometer using 10 mm NMR tubes. IR spectra were measured on a Perkin-Elmer 457 spectrophotometer (in acetone and nujol) and microanalysis were done at the University of Liverpool in U.K.

Addition of 1 mol of Cl_2 or Br_2 to an aqueous solution of 1 mol of $K_2[Pt(CN)_4]$, gave yellow-orange crystalline solids which analyzed for $K[Pt(CN)_4 - Cl(OH_2)]$ (A) and $K[Pt(CN)_4Br(OH_2)]$ (B), respectively. Tetrabutylammonium salt was prepared by addition of NBu_4OH to the above reaction mixtures. This

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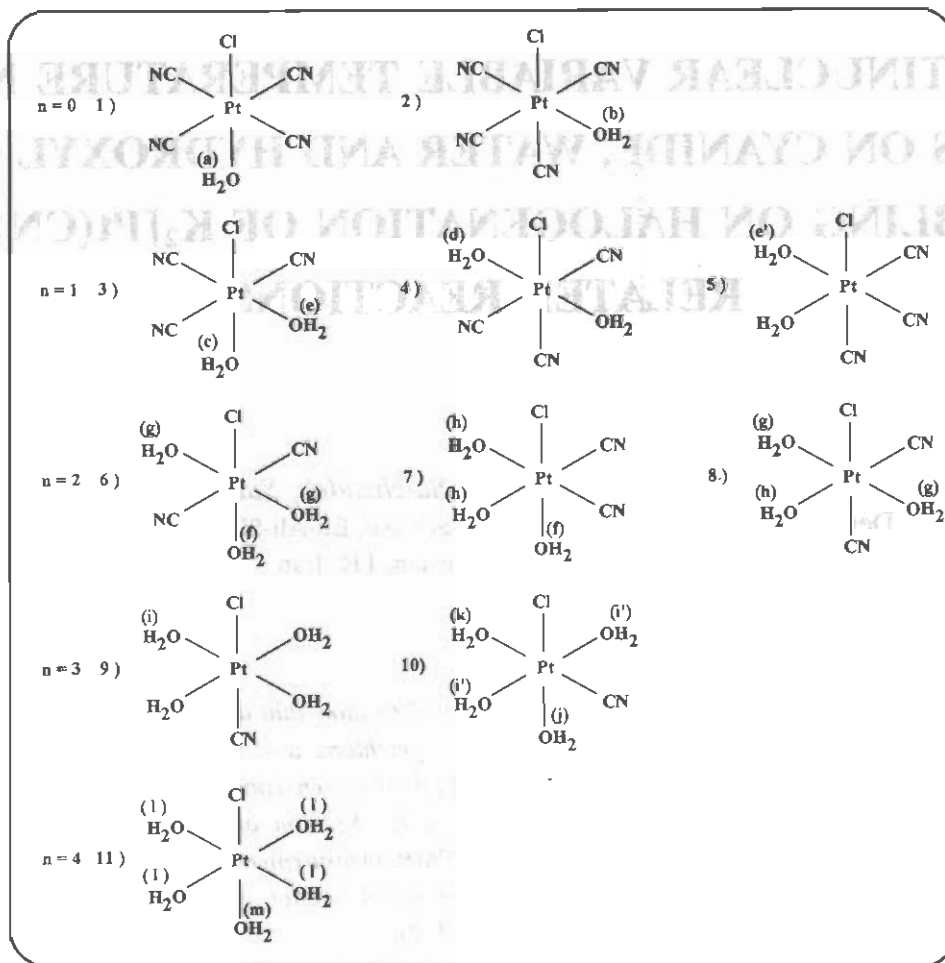


Fig. 1: Structures of eleven complexes of the type $[Pt(CN)_{4-n}Cl(OH_2)_{n+1}]^{(n-1)+}$ ($n = 0, 1, 2, 3, 4$)
 (These structures are also possible for $[Pt(CN)_{4-n}Cl(OH)_{n+1}]^{2-}$ ($n = 0, 1, 2, 3, 4$)).

resulted in >90% yield of $(NBu_4)_2[Pt(CN)_4Cl(OH)]$ (C) and $(NBu_4)_2[Pt(CN)_4Br(OH)]$ (D). The same general procedure was used for the preparation of Pt(IV) complexes containing chloride, bromide, hydroxyl and water molecule [8]. To a solution of $K_2[Pt(CN)_4]$ (0.37 g) in water (20 mL) was added a solution of chlorine (0.6 g) in carbon tetrachloride (5 mL) in presence of perchloric acid (1 M) which was stirred for few minutes. The yellow organic solution was concentrated until a yellow crystalline solid was precipitated which was filtered off and dried in vacuum. Slow addition of 40% NBu_4OH (8 mL) in acetone (5 mL) to the above solution (before concentration) produced an immediate precipitate of C which was recrystallized from acetone-petroleum ether (b.p. 60-80) to give yellow crystals. The

complex C also was prepared via addition of freshly prepared hypochlorous acid (2.94 mL) to the solution of $K_2[Pt(CN)_4]$, (0.534 g) in water (20 mL). The solution was stirred for 10 minutes and treated with NBu_4OH in acetone (8 mL) and yellow precipitate of C appeared which was recrystallized from acetone-petroleum ether to give yellow crystalline solids. Microanalysis data for this complexes are given in Table 4.

RESULTS AND DISCUSSION

^{195}Pt NMR spectrum of A consist of seven lines which are due to the eleven possible species (including isomers) of $[Pt(CN)_{4-n}Cl(OH_2)_{n+1}]^{(n-1)+}$ ($n = 0, 1, 2, 3, 4$) as reported in Table 1 and Fig. 1. The progressive replacement of cyanide by water mole-

Table 1: ^{195}Pt NMR data for $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{H}_2\text{O})_{n+1}]^{(n-1)+}$ ($n=0, 1, 2, 3, 4$) in D_2O .

| n | 0 | 1 | 2 | 3 | 4 | | |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| $\delta_{\text{Pt}}(\text{ppm})^*$ | -5273 | -5255 | -4088 | -2718 | -2002 | -2028 | -1487 |

* Chemical shift internal $\text{H}_2[\text{PtCl}_6]$ with positive shifts being to high frequency.

cules produces a systematic shift to higher frequency (low field) as has been observed for other Pt(II) and Pt(IV) complexes [9, 10, 11]. The separation between these type of geometric isomers in aqueous solution is much less than that observed in other solvents such as acetone- d_6 .

^1H NMR spectrum of A (Fig. 2a) consists of one set of seventeen approximately equally spaced lines, follows from a comparison with systematic trends observed upon substitution of chloride by bromide in $[\text{Pt Br}_x\text{Cl}_{4-x}(\text{PEt}_3)\text{L}]$ ($x=0, 1, 2, 3, 4$), $[\text{Pt Br}_y\text{Cl}_{5-y}(\text{PEt}_3)]^-$ ($y=0, 1, 2, 3, 4, 5$) and $[\text{Pt Br}_{3-a}\text{Cl}_a(\text{PEt}_3)]^-$ ($a=0, 1, 2, 3$) [2,12]. Thus there are seventeen approximately equally spaced resonances due to a progressive replacement of cyanides by water molecules leaving chloride unsubstituted at axial position in octahedral structure, see Table 2, 3 and Fig. 3. This also has been observed in $[\text{Pt}(\text{CN})_5\text{I}]^{2-}$ with exchanging five cyanide ligands in oxidative reaction of $[\text{Pt}(\text{CN})_4]^{2-}$

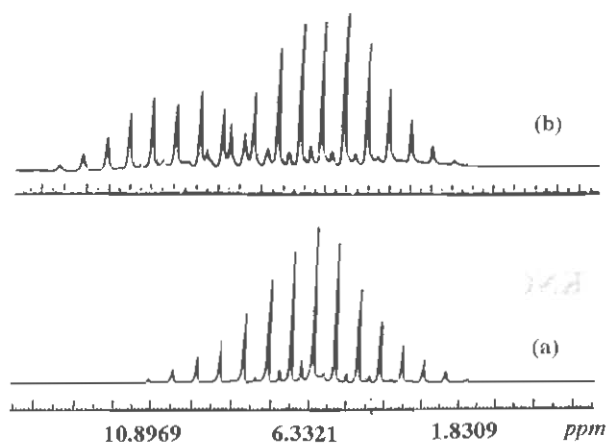


Fig. 2: ^1H NMR spectrum of a) $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{H}_2\text{O})_{n+1}]^{(n-1)+}$ ($n=0, 1, 2, 3, 4$) and b) mixture of $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{OH})_{n+1}]^{2-n-}$ ($n=0, 1, 2, 3, 4$) and $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{OH}_2)_{n+1}]^{(n-1)+}$ ($n=0, 1, 2, 3, 4$) in D_2O and acetone- d_6 respectively.

Table 2: ^1H NMR data for isomers of $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{H}_2\text{O})_{n+1}]^{(n-1)+}$ ($n=0, 1, 2, 3, 4$) in D_2O at 25°C .

| n | Kind of proton | δ_{H}^* (ppm) | $J_{\text{Pt-H}}$ (Hz) |
|---|----------------|-----------------------------|------------------------|
| 0 | a | 1.83 | 101.6 |
| | b | 2.39 | 99.9 |
| 1 | c | 3.52 | 102.5 |
| | d | 4.04 | 102.5 |
| | e | 4.64 | 101.6 |
| | e' | 5.21 | |
| 2 | f | 5.89 | 101.6 |
| | g | 6.23 | 101.6 |
| | h | 6.91 | 101.6 |
| 3 | i | 7.6 | 100.6 |
| | i' | 8.03 | 100.6 |
| | j | 8.60 | 99.6 |
| | k | 9.18 | 100.6 |
| 4 | l | 10.31 | 101.5 |
| | m | 10.89 | 100.6 |

* Chemical shift internal Me_4Si with positive shifts being to high frequency.

with ICN without any exchange in iodide position [13]. In order to account intensities of various complexes we used the Eq. (1):

$$I_2 = \frac{I_1 \cdot p_2 \cdot n_2}{p_1 \cdot n_1} \quad (1)$$

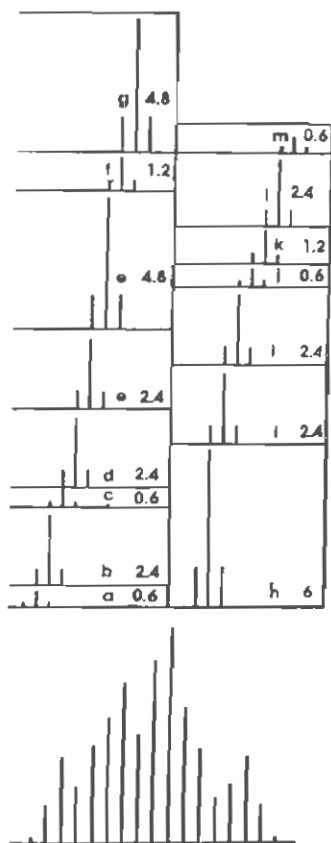
where:

I_1 = total intensity of $[\text{Pt}(\text{CN})_4\text{Cl}(\text{H}_2\text{O})]^-$ (6 m.m),
 I_2 = total intensity of any other species (in m.m),
 p_1 = probability of presence of $[\text{Pt}(\text{CN})_4\text{Cl}(\text{H}_2\text{O})]^- = 1$,
 p_2 = probability of presence of any other species,
 n_1 = number of proton in $[\text{Pt}(\text{CN})_4\text{Cl}(\text{H}_2\text{O})]^- = 1$,
 n_2 = number of equivalent proton in any other species.

Direct integration of resonances due to eleven species in ^1H NMR spectra (Fig. 2) did not correspond to the intensities predicted in Fig. 3 and Table 3. In other words for a statistical scrambling of water and cyanides we would never have the expected and observed equilibrium constant to be exactly the same. Similar results for a statistical scrambling of halogens have been observed [1,12,14]. Similar number of

Table 3: Calculated intensities of ^1H NMR of $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{H}_2\text{O})_{n+1}]^{(n-1)+}$ ($n=0, 1, 2, 3, 4$) with Eq. (1).

| n | Kind of proton | Number of proton(s) | Probability | Total intensity (m.m) | Intensities of triplet (m.m) |
|---|----------------|---------------------|-------------|-----------------------|------------------------------|
| 0 | a | 1 | 1 | 0.6 | 0.1:0.4:0.1 |
| | b | 1 | 4 | 2.4 | 0.4:1.6:0.4 |
| 1 | c | 1 | 1 | 0.6 | 0.1:0.4:0.1 |
| | d | 2 | 2 | 2.4 | 0.4:1.6:0.4 |
| | e | 1 | 4 | 2.4 | 0.4:1.6:0.4 |
| | e' | 2 | 4 | 4.8 | 0.8:3.2:0.8 |
| 2 | f | 2 | 1 | 1.2 | 0.2:0.8:0.2 |
| | g | 4 | 2 | 4.8 | 0.8:3.2:0.8 |
| | h | 2,1 | 4,2 | 6.0 | 1.0:4.0:1.0 |
| 3 | i | 4 | 1 | 2.4 | 0.4:1.6:0.4 |
| | i' | 2 | 2 | 2.4 | 0.4:1.6:0.4 |
| | j | 1 | 1 | 0.6 | 0.1:0.4:0.1 |
| | k | 1 | 2 | 1.2 | 0.2:0.8:0.2 |
| 4 | l | 4 | 1 | 2.4 | 0.4:1.6:0.4 |
| | m | 1 | 1 | 0.6 | 0.1:0.4:0.1 |

Fig. 3: Expected lines for ^1H resonances of $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{H}_2\text{O})_{n+1}]^{(n-1)+}$ ($n=0, 1, 2, 3, 4$).

expected lines in Fig. 3 and observed resonances in Fig. 2a is reached except that two peaks with very low intensities in far and of two sides of spectrum can not be observed.

Variable temperature ^1H NMR spectrum of the non aqueous solution resulting from the addition of NBu_4OH to the A was studied which shows that halogen-hydroxyl group scrambling occurs at various temperatures and spectrum of the eleven possible species due to $[\text{Pt}(\text{CN})_{4-n}\text{Cl}(\text{OH})_{n+1}]^{2-}$ ($n=0, 1, 2, 3, 4$) is very similar to the spectrum of A, Figs. 1 and 2b.

IR spectrum of A and C show of a broad peaks at $2100\text{-}2250$ and 3600 cm^{-1} regions which are due to $\text{-C}\equiv\text{N}$ and -O-H stretching frequencies in these complexes. Broadence of these peaks are due to probably eleven species.

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Table 4: Microanalysis data of prepared complexes.

| Compound | Calculated(%) | | | | Found(%) | | | |
|---------------------------------------------------------------|---------------|-----|------|-----|----------|-----|------|-----|
| | C | H | N | Cl | C | H | N | Cl |
| (NBu ₄) ₂ [Pt(CN) ₄ Cl(OH)] | 51.7 | 8.8 | 10.0 | 4.2 | 52.6 | 8.9 | 10.3 | 4.1 |
| (NBu ₄) ₂ [Pt(CN) ₄ Br(OH)] | 49.1 | 8.3 | 9.5 | — | 49.8 | 8.3 | 9.1 | — |

REFERENCES

- [1] Heaton, B. T. and Kelsey, R. J., *Inorg. Nucl. Chem. Letters*, **11**, 363(1975).
- [2] Heaton, B. T. and Timins, K. J., *J. Chem. Soc. Chem. Comm.*, 931(1973).
- [3] Mason, W. R., *Inorg. Chem.*, **10**, 1914(1971).
- [4] Morgan, K. A. and Jones, M., *J. Inorg. Nucl. Chem.*, **34**, 275(1972).
- [5] Vulik, C. J. and Poe, A., *Inorg. Chim. Acta.*, **34**, 129(1974).
- [6] Drougge, L. and Elding, L. I., *Inorg. Chem.*, **24**, 2292(1985).
- [7] Drougge, L. and Elding, L. I., *Inorg. Chim. Acta.*, **121**, 175(1986).
- [8] Elding, L. I. and Gustafson, L., *Inorg. Chim. Acta.*, **19**, 31(1976).
- [9] Zelewsky, A. V., *Helv. Inorg. Chim. Acta.*, **51**, 803 (1968).
- [10] Mcfarlane, W., *J. Chem. Soc. Dalton*, 324(1974).
- [11] Kenedy, J. D., Mcfarlane, W., Puddephatt, R. J. and Thompson, P. J., *J. Chem. Soc. Dalton.*, 874 (1976).
- [12] Foot, R. J., Ph.D. Thesis, University of Liverpool U.K. (1975).
- [13] Brown, C., Heaton, B. T. and Sabounchei, J. S., *J. Organomet. Chem.*, **142**, 413(1977).
- [14] Ahrland, S., Chatt, J. and Davies, N. R., *Quart. Revs.*, **12**, 265(958).