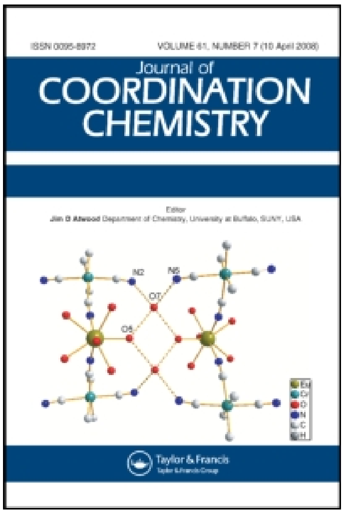

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OXIDATIVE ADDITION OF SOME HALOGENS, INTERHALOGENS AND PSEUDOHALOGENS TO $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$

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The results of the treatment of $[(n-C_4H_9)_4N]_2[Pt(CN)_4]$ with seventeen oxidizing agents, including halogens, inter halogens, and molecules such as N_2O_4, ICN, $(SCN)_2$, $S(CN)_2$ and C_6H_5SCl, are reported. In cases where the reagents were not symmetrical molecules, two different ligands were added to platinum. The competition between parts of the oxidizing agent and other potential ligands in solution is also examined.

INTRODUCTION

Earlier, we reported the oxidative addition of a number of halogen, interhalogen, and pseudohalogen molecules to platinum compounds, $Pt(phen)X_2$ (phen = 1, 10-phenanthroline, X = Cl, Br, or I).[1] Unlike some oxidative addition reactions of iridium(I), the added ligands were shown to be trans to each other in the product. An interesting aspect of the reactions was the discovery that the second ligand added to platinum(II) was not necessarily part of the oxidizing agent. For example, when bromine was used as an oxidizer in the presence of a large excess of chloride, the product has a stoichiometry as if it had been prepared with BrCl. This product was rationalized on the basis of the mechanism for platinum(II) oxidative addition reactions proposed by Jones and Morgan.[2] An unanticipated result of the research was that, although a stoichiometric amount of I_2 resulted in the addition of two iodide ligands, an excess of reagent gave additional iodine uptake, yielding compounds of the formula $Pt(phen)Cl_2I_6$, $Pt(phen)Br_2I_4$, and $Pt(phen)I_6$. We interpreted the compounds as containing triiodide (or iodide and triiodide ligands) bound to platinum(IV), but a recent structural study of $Pt(phen)I_6$[3] leaves no doubt that only iodide ligands are present and that the excess iodine exists as I_2 molecules forming bridges between iodide ligands in different $Pt(phen)I_4$ units.

Although reagents such as ICI, ICN, and $(SCN)_2$, were successfully added to platinum(II) for the first time, a disappointment in the research was that others, including methyl iodide, hydrogen chloride, and even hydrogen peroxide which had been used successfully before on platinum(II),[4] left $Pt(phen)X_2$ compounds unchanged. In the hope of widening the range of reagents that would react with platinum(II) and facilitating the characterization of the products, the present research was initiated using tetra-n-butylammonium tetracyanoplatinate(II) as the source of metal. This material was seen to have three advantages over the $Pt(phen)X_2$ compounds. First it might be more reactive because it is soluble in organic solvents such as methylene chloride, which are inert to most oxidizing agents of interest. The phenanthroline complex was insoluble in all solvents in which it was stable, necessitating its introduction as a slurry. Second, the products, unlike the phenanthroline-containing products, were also expected to be soluble, greatly simplifying the recording of spectra and other characteristics. Finally, according to the kinetics study,[2] a complex is formed between the oxidizing agent and the platinum(II) compound prior to oxidation. In this interaction the oxidizing agent appears to act as a Lewis acid. A negative charge on the metal compound might facilitate complex formation and so increase reactivity.

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†Deceased.

EXPERIMENTAL

Tetra-n-butylammonium tetracyanoplatinate(II), $[(C_4H_9)_4N]_2[Pt(CN)_4]$, was prepared as reported by Gray.[5] Anal. Calcd for $PtC_{36}H_{72}N_6$: Pt, 24.9. Found: Pt, 24.6.

Tetra-n-butylammonium dichlorotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4Cl_2]$. Commercial NOCl was passed through a trap immersed in a Dry Ice-acetone bath and into CH_2Cl_2 (30 ml) at 0° for a few minutes. The solution was added to another of $[Bu_4N]_2[Pt(CN)_4]$ (0.3 g) in CH_2Cl_2 at the same temperature. The resulting solution was stirred for 1.5 hours while being protected from contact with air. The volatiles were pumped off leaving the dichloro salt as a residue. Final drying was carried out at 80° in a vacuum. *Anal.* Calcd for $PtC_{36}H_{72}N_6Cl_2$: Pt, 22.9, C; 50.6: H, 8.4; N, 9.8; Cl, 8.3. Found: Pt, 22.8; C, 50.8; H, 8.5; N, 10.1; Cl, 8.4.

Tetra-n-butylammonium dibromotetracyanoplatinate (IV), $[(C_4H_9)_4N]_2[Pt(CN)_4Br_2]$. The tetracyanoplatinate(II) complex (1.0 g) was dissolved in CH_2Cl_2 (50 ml). About one gram of Br_2 was added, and, after the reaction had been stirred at room temperature for 10 minutes, the solvent and excess Br_2 were removed by evaporation. The residue was recrystallized from equal parts of water and acetone. The yellow product was washed with ether and dried in a vacuum. *Anal.* Calcd for $PtC_{36}H_{72}N_6Br_2$: Pt, 20.7; C, 45.8; H, 7.7; N, 8.9; Br, 16.9. Found: Pt, 20.5; C, 45.8; H, 7.7; N, 8.7; Br, 17.2.

Tetra-n-butylammonium diiodotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4I_2]$. The tetracyanoplatinate(II) complex (0.20 g) and I_2 (1.0 g) were refluxed in CH_2Cl_2 (30 ml) for 20 hr. The volatile components were evaporated in a stream of N_2. The residue was recrystallized from acetone diethyl ether, giving golden yellow crystals. *Anal.* Calcd for $PtC_{36}H_{72}N_6I_2$: Pt, 18.8; C, 41.7; H, 7.0; N, 8.1; I, 24.5. Found: Pt, 18.3; C, 41.7; H, 7.2; N, 8.1; I, 24.4

Tetra-n-butylammonium bromoiodotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4BrI]$. To a solution of the tetracyanoplatinate(II) salt (0.25 g) in CH_2Cl_2 was added to a two-fold excess of IBr (0.13 g). The reaction mixture was stirred for 2 hr, and the residue from the evaporation of the volatiles was washed several times with ether. The orange product was dried in a vacuum. *Anal.* Calcd for $PtC_{36}H_{72}N_6IBr$: Pt, 19.7; C, 43.7; H, 7.3; N, 8.5. Found: Pt, 20.0; C, 44.0; H, 7.4; N, 8.7.

Tetra-n-butylammonium dithiocyanatotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4(SCN)_2]$. To a solution of the diiodotetracyanoplatinate(IV) salt (0.10 g) in CH_2Cl_2 (20 ml) a considerable excess of AgSCN (0.5 g) was added and the resulting slurry was kept well stirred for 4 hr. The reaction mixture was filtered through a fine frit, and the filtrate was evaporated to dryness giving a yellow product which was washed several times with ether and dried in a vacuum desiccator. *Anal.* Calcd for $PtC_{38}H_{72}N_8S_2$: Pt, 21.7; C, 50.7; H, 8.0; N, 12.5; S, 7.1. Found: Pt, 21.7; C, 50.7; H, 8.1; N, 12.5; S, 7.0. An attempt to prepare this product by the oxidative addition of thiocyanogen to $Pt(CN)_4{}^{2-}$ was unsuccessful.

Tetra-n-butylammonium dinitrotetracyamoplatinate(IV), $[(C_4H_9)N]_2[Pt(CN)_4(NO_2)_2]$. Commercial nitrogen dioxide was condensed into a tube using a Dry Ice-acetone bath. The tube was slowly warmed, and the NO_2 was led into CH_2Cl_2 (30 ml) to form a saturated solution was added to the tetracyanoplatinate(II) salt (0.30 g) in CH_2Cl_2 (30 ml). After standing an hour at room temperature, the volatiles were removed. The residue was slurried with water, filtered and washed several times with ether. *Anal.* Calcd for $PtC_{36}H_{72}N_8O_4$: Pt, 22.3; C, 49.4; H, 8.2; N, 12.8; O, 7.3. Found: Pt, 22.0; C, 49.8; H, 8.4; N, 12.5; O, 7.2.

Tetra-n-butylammonium iodopentacyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_5I]$. The tetracyanoplatinate(II) salt (0.4 g) was refluxed with an excess (0.5 g) of ICN in CH_2Cl_2 (30 ml). The solvent was evaporated and the residual ICN was removed by repeated washings with ether. The yellow product was dried in a vacuum. *Anal.* Calcd for $PtC_{37}H_{72}N_7I$: Pt, 20.8; C, 47.4; H, 7.7; N, 10.5; I, 13.6. Found: Pt, 20.9; C, 47.7; H, 7.7; N, 10.5; I, 13.5.

Tetra-n-butylammonium bromochlorotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4ClBr]$. The tetracyanoplatinate(II) salt (0.2 g) was dissolved in CH_2Cl_2. Hydrogen chloride which had been dried using H_2SO_4 was bubbled in. When the solution had become saturated with HCl, exactly one mole equivalent of bromine (as a 0.1 M solution in CH_2Cl) was added using a burette. The reaction was allowed to proceed two minutes while a yellow suspension was formed. Volatile components were removed on a waterbath, and the residue was recrystallized from acetone-diethyl ether. *Anal.* Calcd for $PtC_{36}H_{72}BrCl$: Pt, 21.7; C, 48.1; H, 8.0. Found: Pt, 21.4; C, 47.8; H, 7.9.

Tetra-n-butylammonium chloroiodotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4ClI]$. The tetracyanoplatinate(II) salt (0.5 g) was dissolved in CH_2Cl_2 and freshly prepared ICl was added a little at a time until the solution turned a deep orange-red. After an hour at room temperature, the solution was evaporated to dryness, and the residue was washed with ether and dried in a vacuum, giving a golden yellow solid. *Anal.* Calcd for $PtC_{36}H_{72}ClI$: Pt, 20.6; C, 45.7; H, 7.6; N, 8.9; Cl, 3.8; I, 13.4. Found: Pt, 20.7; C, 45.6; H, 7.8; N, 8.8; Cl, 3.6; I, 13.6.

Tetra-n-butylammonium phenylsulfidochlorotetracyanoplatinate(IV), $[(C_4H_9)_4N]_2[Pt(CN)_4(SC_6H_5)Cl]$. The tetracyanoplatinate(II) salt (0.300 g) was dissolved in carefully dried CH_2Cl_2 (30 ml). A slight excess of C_6H_5SCl[6] (0.071 g) in CH_2Cl_2 was introduced through a serum cap. The solution became red-orange, and after 10 min at room temperature, a stream of N_2 was blown through the reaction vessel to remove the solvent. The orange product was recrystallized from acetone-diethyl ether. *Anal.* Calcd for $PtC_{42}H_{77}N_6ClS$: Pt, 21.0; C, 54.3; H, 8.3; N, 9.1; Cl, 3.8; S, 3.5. Found: Pt, 21.0; C, 54.6; H, 8.4; N, 9.0; Cl, 3.7; S, 3.4.

Elemental analyses for platinum were carried out by combustion; other elements were determined by Huffman Laboratories, Inc., Wheatridge, Colorado.

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Samples were prepared as KBr discs. Wavelength readings were calibrated using a polystyrene standard.

RESULTS AND DISCUSSION

Several new tetracyanoplatinate(IV) salts have been prepared. Among the types $[Bu_4N]_2[Pt(CN)_4X_2]$ were X = halide, the dichloro complex was prepared using NOCl as the oxidizing agent. This product resulted from an attempt to prepare the $[Pt(CN)_4(NO)Cl]^{2-}$ ion. Few platinum(IV) nitrosyls are well characterized, and our experience with the $Pt(phen)X_2$ compounds[1] indicated that nitrosyl ligands were being added, but pure compounds were not obtained. The bromide and iodide complexes were prepared directly with the halogens. The anions had been reported before[7] as the potassium salts. Because for $Pt(phen)X_2$, complexes appearing to contain iodine in excess of that needed for simple oxidation had been formed using excess iodine reagent, attempts were made to obtain similar results in this research. With a large quantity of iodine, a red-brown compound of the composition $[Bu_4N]_2[Pt(CN)_4I_{3.2}]$ was obtained. Recrystallization from benzene-acetone converted this material to the diiodo complex, so if excess iodine were present in the impure compound, it was unstable under rather mild manipulation.

Unsymmetrical halogen addition, that is, the synthesis of $[Bu_4N]_2[Pt(CN)_4XY]$, where X and Y are different halo ligands, were carried out in two ways. ICl and IBr were all behaved as reagents and when carefully purified gave respectively the iodochloro and the iodobromo complexes. BrCl is not readily available, and the bromochloro complex was prepared by adding one equivilent of bromine to $[Bu_4N]_2[Pt(CN)_4]$ dissolved in CH_2Cl_2 saturated with HCl. According to the work of Jones and Morgan,[2] this reaction is successful because the addition of halogen is not concerted. Instead bromine forms a complex $[Pt(CN)_4(Br)S]^+$ (where S is a solvent molecule) plus a bromide ion (see Figure 1). If bromine is the only reagent present, the bromide ion formed will displace the solvent molecule to give the dibromo compound. If other potential ligands are present in solution, however, there will be a competition in which the nature of the product will be determined by the relative concentrations and nucleophilicities of the competing species. There is reason to think that the product is not necessarily the

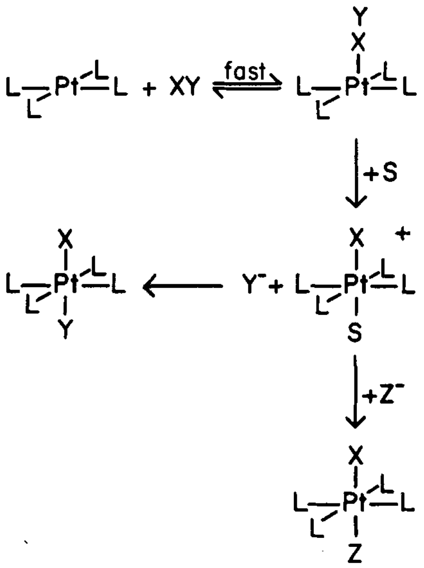

FIGURE 1 Mechanism for the oxidative addition of XY to $Pt(CN)_4{}^{2-}$. The final step shows the competition between Y^- and another ligand, Z^-, for a position in the coordination sphere of platinum(IV).

thermodynamically favored one. Although concentration outweighed nucleophilicity in the case mentioned here, great differences in nucleophilicity will prevent the successful application of this method; attempts to prepare the iodochloro complex form one equivalent of iodine in excess hydrogen chloride invariably gave products with more than the desired amount of iodide.

Other molecules added to $[Bu_4N]_2[Pt(CN)_4]$ were N_2O_4, ICN, and $(SCN)_2$. The reactions proceeded smoothly, but in the case of thiocyanogen an alternative route was used to obtain a pure product. The problem arose because thiocyanogen polymerizes during the course of the reaction to give an orange product that could not be separated from the platinum compound. The dithiocyanato complex was prepared by the reaction of $[Bu_4N]_2[Pt(CN)_4I_2]$ with AgSCN.

Several attempts at oxidative additions with other reagents failed. It has already been mentioned that NOCl gave the dichloro instead of the chloronitrosyl compound, but this may have been the result of having an excess of reagent. Cyanogen bromide seemed to go only part way to completion, and the use of one equivalent of Br_2 in the presence of HCN gave the dibromo compound. Under the usual conditions, CH_3I gave no reaction, whereas long refluxing of $[Bu_4N]_2[Pt(CN)_4]$ in pure CH_3I gave a precipitate which contained no n-butylammonium groups but was not further characterized. CH_3SSCH_3 and NO_2PF_6 also gave uncharacterized decomposition products. H_2O_2, $(CN)_2$, and $S(CH)_2$ were unreactive toward the tetracyano compound.

The Table shows the frequencies of infrared absorptions assigned by Jones and Smith to the E_u cyanide stretching mode (ν_{16}).[8] For the dichloro and dibromo complexes our frequencies lie some 13 cm^{-1} below those previously reported, although the difference in frequencies is exactly the same in both studies. This may be the result of the difference in cations and in the way in which the samples were prepared for spectroscopic analysis. The difference between the diiodo compounds does not run parallel, however, being only 4 cm^{-1}, which is not surprising in view of the fact that the compound described by Jones and Smith was almost black, whereas ours was dark yellow. The entries in the Table are in order of increasing frequency, and it may be seen that bromide lies between chloride and iodide and that the mixed dihalogens are nearly in the order expected. The series reflects increasing strength of the C–N bond. What property or properties of the axial ligands contributes to this change cannot be stated with certainty. Among the types of rankings in which ligands are marshalled, that of the kinetic trans effect[9] is clearly the wrong order. Common listings of the spectro-chemical series[10] seem to give reasonable agreement. This order holds for platinum(IV), at least as far as the halide ligands are concerned.[11] Perhaps stronger axial ligands decrease the binding between platinum and cyanide, resulting in less delocalization of platinum electron density into the cyanide π^* orbitals and so increasing the C–N bond strength.

TABLE I
Frequencies of the E_u cyanide stretching mode of the compounds $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4XY]$

X	Y	$\nu(cm^{-1})$
I	I	2157
I	Cl	2158
I	Br	2159
Br	Br	2160
C_6H_5S	Cl	2161
Br	Cl	2162
Cl	Cl	2164
I	CN	2166
SCN	SCN	2166
NO_2	NO_2	2169

While several new compounds were prepared from $[Bu_4N]_2[Pt(CN)_4]$, it could not be stated that the increased negative charge on the complex ion or its increased solubility appeared to enhance its reactivity compared with the neutral, insoluble $Pt(phen)X_2$ compounds. Our interpretation of the charge effect on reactivity appears to have been in error, and it may be that greater reactivity will arise from a positive rather than a negative charge on the reagent complex.

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