

complex, but it reacts much faster than the molybdenum hexacarbonyl or the MR_3 carbonyl derivatives. To the extent that such effect, as observed, is attributable to a stronger Mo-C bond in the starting complex, one can surmise that it results from a rather delicate balance of σ -donating and π -accepting abilities of the coordinated ligands not yet fully understood. The relative importance of the steric and electronic properties of ligand L in determining the *cis* effect seems to depend on the metal atom also. Further testing of this observation was not feasible since rates of reactions analogous to that represented by eq 1 for chromium and tungsten carbonyl derivatives were too slow to be measured.

As for the k_2 term, the reactivity order for the reactions of $Mo(CO)_5(4\text{-pic})$ is 3,4-lutidine > 4-picoline > 3-chloropyridine, reflecting the decreasing proton basicity order of these amines. Such correlation between nucleophilic reactivity and proton basicity has long been recognized as a general feature of bimolecular substitution on carbonyl derivatives, among which tetracarbonyl halide dimers of rhenium and manganese, $[M(CO)_4X]_2$, might be mentioned.^{6,16} The extremely low reactivity of $Mo(CO)_5MR_3$ is likely to be due to steric hindrance to bimolecular attack of the bulky reagent species.

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Some Properties of Several Trimethylplatinum(IV) Compounds

BY G. R. HOFF AND C. H. BRUBAKER, JR.

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Trimethylplatinum(IV) iodide was first prepared in 1909 by Pope and Peachey,¹ and later Menzies and Overton² reported that a yellow form of the compound was tetrameric in benzene but that the white form, which they prepared by adding potassium iodide to a solution of trimethylplatinum(IV) sulfate, was dimeric. The crystal structure of trimethylplatinum(IV) chloride was determined by Rundle and Sturdivant,³ and it was also tetrameric. Trimethylplatinum(IV) compounds such as the hydroxide, nitrate, and sulfate¹ have been reported.⁴⁻⁶ In this laboratory⁷

we have been interested in trimethylplatinum compounds in connection with unsuccessful attempts to prepare tetramethylplatinum(IV) by the reaction of methylsodium with trimethylplatinum(IV) iodide.⁸ The present note deals with the question of possible differences between the yellow and white forms of the trimethylplatinum(IV) iodide and the conductances of trimethylplatinum(IV) salts in aqueous solutions.

Experimental Section

Yellow $(CH_3)_3PtI$ was prepared by the method of Clegg and Hall,⁹ the sulfate, and the white form of $(CH_3)_3PtI$ were prepared by the methods of Pope and Peachey¹ and Ivanova and Gel'man.⁵

Infrared spectra were determined by use of KBr disks, mineral oil, Fluorolube, and 1,3-hexachlorobutadiene mulls. A Unicam SP-200 spectrophotometer was used for the 650–5000- cm^{-1} region and a Beckman IR-7 spectrophotometer for the 200–650- cm^{-1} region.

X-Ray powder diffraction patterns were obtained with samples in 0.3-mm glass capillary tubes, a copper X-ray tube with nickel filter, and a 114.59-mm camera.

Molecular weights of the two forms of the $(CH_3)_3PtI$ were determined in benzene by use of a Mechrolab vapor pressure osmometer and a nonaqueous probe designed to operate at 37°. It was calibrated with benzil as a standard.

Conductance measurements of $(CH_3)_3PtNO_3$ and $[(CH_3)_3Pt]_2SO_4$ solutions in water were made by use of a Wayne-Kerr B221 Universal bridge and a modified Shedlovsky cell.¹⁰ The $[(CH_3)_3Pt]_2SO_4$ was weighed as the tetrahydrate and portions were added successively to the cell which contained a known volume of water. Since the nitrate was deliquescent, it could not be weighed and introduced into the cell, but a concentrated solution was prepared by quantitative metathesis between a solution of known concentration of the sulfate and barium nitrate. The conductance of concentrated stock solution, in which the platinum content had been determined, was measured and it was diluted successively to make the more dilute solutions.

Results and Discussion

The first objective of this study was to compare the yellow and white forms of trimethylplatinum(IV) iodide and no differences could be found. The infrared spectra proved to be identical and the absorptions found compared very well with those previously reported for the yellow form.^{7,11} A few minor differences were observed in the X-ray diffraction powder patterns, but they consisted only of an absence of a few very weak lines from one or the other pattern. The patterns compared favorably with that previously reported for the yellow form⁷ (Table I).

Menzies and Overton² had determined the molecular weight of the iodides in benzene and reported association factors of 3.2–3.4 for the yellow form and 2.4 for the white form and they noted the white was converted to the yellow upon standing in warm or boiling benzene. In this study we have determined the association factors and find 4.01 ± 0.12 for the yellow form and 4.07 ± 0.08 for the white form. The yellow form is recovered if the solution of the white form is refluxed with benzene and then concentrated until crystallization occurs.

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TABLE I
X-RAY POWDER DIFFRACTION DATA
(d VALUES IN Å)

(CH ₃) ₃ PtI		[(CH ₃) ₃ Pt]- SO ₄	(CH ₃) ₃ Pt- NO ₃
Yellow form	White form		
		11.30 s	5.91 m
		10.40 s	5.72 s
		6.41 vw	5.26 s
		6.17 m	4.64 s
		5.55 vs	4.03 m
		5.27 vs	3.81 w
		5.05 s	3.61 w
		4.91 s	3.30 w
		4.45 m	3.23 w
		4.18 w	3.17 w
		3.38 vw	2.95 vw
		3.58 vw	2.90 vw
		3.42 vw	2.85 w
		3.38 m	2.78 vw
		3.26 m	2.74 w
		3.05 s, b	2.70 vw
		2.84 vw	2.51 vw
		2.73 m	2.47 vw
		2.68 s	2.44 s
		2.53 vw	2.34 m
		2.47 m	2.30 w
		2.43 m	2.20 w
		2.40 vw	2.15 w
		2.35 w	2.07 vvw
		2.29 w	2.02 m
		2.20 w	1.98 w
		2.15 s	1.93 w
		2.08 vw	1.86 m
		2.03 w	1.83 m
		1.99 w	1.81 m
		1.96 m	1.65 m
		1.90 vw	1.59 vw
		1.87 w	1.56 m
		1.80 w	1.52 vw
		1.73 m	1.47 vvw
		1.66 vw	1.45 vw
		1.62 w	1.43 vw
		1.60 w	1.37 s
		1.58 w	1.35 m
		1.56 w	1.28 w
		1.54 w	1.24 m
		1.50 w	1.14 w
		1.48 vw	1.04 w
		1.43 w, b	
		1.40 vw	
		1.38 cw	
		1.35 w	
		1.34 w	
		1.30 w, b	
		1.25 vw	
8.59 m	8.60 w		
8.13 s	8.15 s		
7.74 m	7.75 m		
7.24 m	7.26 m		
6.32 s	6.30 s		
5.06 w	5.07 w		
4.61 w	4.64 w		
4.36 w	4.34 w		
...	4.04 vw		
3.79 vw	3.79 vw		
3.67 vw	...		
3.43 vw	3.47 vw		
3.33 vw	3.34 vw		
3.22 w	3.23 s		
3.14 s	3.15 m		
3.03 m	3.05 m		
2.98 m	...		
2.91 m	2.91 s		
2.83 m	2.82 s		
2.69 vw	...		
2.62 w	2.62 w		
2.57 vw	2.57 vw		
2.54 vw	...		
2.49 vw	2.49 s		
2.41 s	2.41 m		
2.38 vw	...		
2.36 vw	2.36 m		
2.30 w	2.30 vw		
2.22 w	2.22 w		
2.20 w	2.19 m		
2.16 w	...		
2.11 w	2.10 w		
2.05 m	2.06 w		
2.03 vw	2.03 vw		
1.98 m	1.97 m		
1.89 vw	1.90 w		
1.88 vw	...		
1.87 vw	1.86 w		
1.84 vw	...		
1.78 vw	1.76 vw		
...	1.73 vw		
...	1.71 vw		
...	1.65 vw		
1.62 vw	1.62 vw		
1.60 vw	1.60 vw		
	1.58 vw		
	1.55 vw		

It appears that the white and yellow forms are identical, except for some minor impurity, possibly iodine. It was not possible to isolate the impurity, although, when yellow (CH₃)₃PtI is converted to the sulfate or is dissolved in benzene, a small dark residue remains. We were unable to collect enough of the residue to analyze. The yellow compound can be whitened considerably if a benzene solution is treated with a silver salt and the trimethylplatinum(IV) iodide is recovered.

Clegg and Hall,¹² Glass and Tobias,¹³ and Kite, *et al.*,⁶ have concluded that the trimethylplatinum(IV) ion is unassociated and octahedral in water and our conductance data agree to the extent that (CH₃)₃PtNO₃ is a strong 1-1 electrolyte and [(CH₃)₃Pt]₂SO₄ is a typical 1-2 sulfate. The Λ_0 values were determined by extrapolation by the method of Owen,¹⁴ and the method of least squares was employed in fitting the data. The conductance results are given below.

$N \times 10^3$ and Λ (ohm⁻¹ cm² equiv⁻¹) for (CH₃)₃Pt-

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NO₃: 38.32, 95.4; 33.53, 96.7; 25.67, 98.8; 22.46, 99.8; 19.65, 100.7; 14.74, 102.6; 11.05, 104.2; 7.254, 106.0; 6.346, 106.6; 5.553, 107.0; 4.858, 107.6; 4.251, 108.0; 3.188, 108.9; 2.390, 109.6; 0.840, 111.4; 0.525, 112.1; $\Lambda_0 = 114.3 \pm 0.06$.

$N \times 10^3$ and Λ (ohm⁻¹ cm² equiv⁻¹) for [(CH₃)₃Pt]₂-SO₄: 24.44, 86.8; 22.22, 88.1; 18.14, 90.4; 15.68, 92.0; 10.87, 95.6; 8.804, 97.5; 7.120, 99.0; 6.346, 99.9; 5.334, 101.1; 4.870, 101.6; 3.528, 103.5; 3.004, 104.5; 2.478, 105.5; 1.981, 106.6; 1.610, 107.4; 1.051, 109.0; $\Lambda_0 = 117.5 \pm 0.09$.

Infrared spectra of the nitrate and sulfate agree with those previously reported^{15,16} when they are measured in mulls, but in KBr disks only the spectrum of (CH₃)₃-PtBr is observed.

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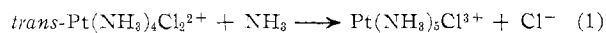
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The Interconversion of the *trans*-Dichlorotetraammineplatinum(IV) and *trans*-Chloropyridinetetraammineplatinum(IV) Cations

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A variety of substitution reactions of *trans*-Pt-(NH₃)₄Cl₂²⁺ and similar complexes are catalyzed by Pt(NH₃)₄²⁺ and have been postulated to proceed *via* an inner-sphere redox mechanism.¹ Zvyagintsev and Shubochkina however have reported that the rates of reactions of a number of such complexes with ammonia and pyridine are unaffected by the addition of Pt-(NH₃)₄²⁺.² One reaction (1) on which they reported



has been restudied.³ The results indicated that reaction 1 is catalyzed by Pt(NH₃)₄²⁺ and does not proceed cleanly in the basic solutions used in ref 2.

The present study was initiated in order to determine whether the results reported in ref 2 for reaction 2

$$\text{trans-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+} + \text{py} \longrightarrow \text{trans-Pt}(\text{NH}_3)_4\text{pyCl}^{3+} + \text{Cl}^- \quad (2)$$

are valid (py = pyridine). In the earlier study of this reaction, the products were not characterized and the pH was not controlled.

Experimental Section

The preparation and analyses of *trans*-[Pt(NH₃)₄Cl₂](NO₃)₂ and [Pt(NH₃)₄](ClO₄)₂ have been described in an earlier paper.³

Preparation of *trans*-[Pt(NH₃)₄pyCl](NO₃)₃.—One gram (2.16

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