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Reaction of Azide Ion with *trans*-Dichlorotetraammineplatinum(IV) Cations. Synthesis of Chloroazidotetraammineplatinum(IV) Salts

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The new complexes *trans*-$[Pt(NH_3)_4ClN_3]Cl_2$ and *trans*-$[Pt(en)_2ClN_3]Cl_2$ were prepared and characterized. Kinetic studies demonstrated that for the preparation of the ammonia complex at 25° and ionic strength 0.23 the rate equals $39[Pt(NH_3)_4Cl_2^{2+}][Pt(NH_3)_4^{2+}][N_3^-]$; for the ethylenediamine complex at 25° and ionic strength 0.40 the rate equals $120[Pt(en)_2Cl_2^{2+}][Pt(en)_2^{2+}][N_3^-]$. Subsequent reaction with additional azide ion is very slow. This suggests that azide ion is ineffective as a bridging ligand for two-electron inner-sphere redox reactions and supports a previous proposal that in similar reactions thiocyanate bridges only through the sulfur atom.

Introduction

Substitution reactions of platinum(IV) complexes which are catalyzed by appropriate platinum(II) complexes have been extensively studied.[2] The mechanism proposed for these reactions involves an inner-sphere redox step in which one ligand of the platinum(IV) complex becomes bonded to the platinum(II) catalyst.[3] Studies on the effectiveness of ligands as bridging groups in these reactions of platinum(IV) have established this order: I >> Br > –SCN > Cl. No data to support the ability of OH, NO_2, or NH_3 to act as a bridge in platinum(IV)–platinum(II) redox reactions have been reported. If any of these can serve this function, it is much less effective than Cl.

In the platinum(IV) substitution reactions in which thiocyanate is thought to act as the bridging group,[4] the bridging was said to occur through the sulfur atom alone. Evidence cited was the relatively fast rate of the reaction and the inability to detect a Pt–NCS linkage during or after the reaction. Studies on the related ligand azide ion, N_3^-, could provide support for this claim. The behavior of azide and thiocyanate ions as bridging ligands in one-electron inner-sphere redox reactions involving light transition metals has been the subject of a number of articles.[5] A contrast with the two-electron platinum system is of interest.

Results and Discussion

Rate data on reactions 1 and 2 were collected (en represents

$$trans\text{-}Pt(NH_3)_4Cl_2^{2+} + N_3^- \rightarrow trans\text{-}Pt(NH_3)_4ClN_3^{2+} + Cl^- \tag{1}$$

$$trans\text{-}Pt(en)_2Cl_2^{2+} + N_3^- \rightarrow trans\text{-}Pt(en)_2ClN_3^{2+} + Cl^- \tag{2}$$

ethylenediamine). The products of the reactions had not been previously known. Therefore both were synthesized and characterized. The products have intense absorption maxima at 268 nm ($\epsilon(Pt(NH_3)_4ClN_3^{2+})$ 1.1 × 10^4, $\epsilon(Pt(en)_2ClN_3^{2+})$ 1.06 × 10^4) whereas the dichloro reactants have maxima at 259 nm with molar absorptivities (ϵ's) less than 1000. The characteristic absorption at 268 nm was used to follow the progress of the reactions and was used as an assay of completeness of reactions and purity of products. The spectra of "infinite-time" solutions of kinetic runs matched those of corresponding solutions of the independently synthesized products. Aqueous solutions of the azidochloro complexes slowly decompose. The 268-nm maximum decreases by a few percent a day at 25°, a decrease which is enhanced by light or the addition of a base. The azidochloro compounds react with chloride ion to regenerate the starting material; however the equilibrium lies far in favor of the azide complexes and reactions 1 and 2 are much faster in the forward than in the reverse directions.

Table I. Rate Data

trans-$Pt(NH_3)_4Cl_2^{2+} + N_3^- \rightarrow$ *trans*-$Pt(NH_3)_4ClN_3^{2+} + Cl^-$

$10^4[Pt(NH_3)_4^{2+}]$, M	$[N_3^-]$, M	k_3,[a] M^{-2} sec^{-1}	$10^4[Pt(NH_3)_4^{2+}]$, M	$[N_3^-]$, M	k_3, M^{-2} sec^{-1}
	15.0°			35.0°	
4.53	0.050	24	4.45	0.025	60
9.1	0.050	25	8.9	0.025	58
17.6	0.050	27	17.8	0.025	58
	25.0°			45.0°	
4.45	0.050	40	2.22	0.025	86
8.9	0.050	39	4.45	0.025	84
17.8	0.050	35	8.9	0.025	79
4.45	0.10	40			
8.9	0.10	38			
17.8	0.025	40			
8.9	0.050	22[b]			

trans-$Pt(en)_2Cl_2^{2+} + N_3^- \rightarrow$ *trans*-$Pt(en)_2ClN_3^{2+} + Cl^-$

$10^4[Pt(en)_2^{2+}]$, M	$[N_3^-]$, M	k_3,[c] M^{-1} sec^{-1}	$10^4[Pt(en)_2^{2+}]$, M	$[N_3^-]$, M	k_3, M^{-1} sec^{-1}
	5.0°			25.0°	
2.0	0.040	18.6	1.00	0.040	75
4.0	0.040	18.1	2.0	0.040	68
8.0	0.040	18.4	4.0	0.040	61
	15.0°		2.0	0.040	88[d]
			1.07	0.050	122[e]
1.0	0.040	35	1.07	0.101	118[e]
2.0	0.040	35	1.07	0.152	123[e]
4.0	0.040	34			
8.0	0.040	33			

[a] [*trans*-$Pt(NH_3)_4Cl_2^{2+}$] = 1.45 × 10^{-4} M, ionic strength 0.23 (maintained with $NaClO_4$); $\Delta H^\ddagger = 6.8 \pm 0.4$ kcal/mol; $\Delta S^\ddagger = -28 \pm 2$ cal/(mol deg). [b] Ionic strength 0.050. [c] [*trans*-$Pt(en)_2Cl_2^{2+}$] = 1.02 × 10^{-4} M, ionic strength 0.040; $\Delta H^\ddagger = 10 \pm 2$ kcal/mol; $\Delta S^\ddagger = -17 \pm 4$ cal/(mol deg). [d] $[NaClO_4] = 0.080$ M. [e] Ionic strength 0.40 (maintained with $NaClO_4$).

Rate data for reactions 1 and 2 are reported in Table I. The rate data were analyzed in terms of the rate law (3). The

$$-d[Pt(IV)]/dt = k_3[Pt(IV)][Pt(II)][N_3^-] \tag{3}$$

rate dependence on the concentration of platinum(II) catalyst for both reactions, particularly at the higher temperatures, shows trends which may indicate that a platinum(II)-independent term should be added to the rate law. Its contribution would be small, and we feel that the analysis excluding this term is probably more representative of the systems. A platinum(II)-independent term could reflect the presence of a small amount of platinum(II) in the platinum(IV) reactant, platinum(II) generated by decomposition of platinum(IV) complexes, or a truly platinum(II)-independent process.

The pH of the kinetic solutions was in the 7–8 range. In order to check whether hydrolysis of the azide product influences the data reported, runs were made in which perchloric acid was added to adjust the pH to 5.4. The rate constants were unchanged (after a correction was made for the N_3^- which was converted to HN_3). However the total absorbance change during these runs was several percent greater than in other experiments. This indicates that in slightly alkaline solution an additional reaction occurs which lowers the absorbance at 270 nm.

The rate of both reactions 1 and 2 increases as the ionic strength is raised. Activation parameters were evaluated from the temperature-dependence data and are cited in footnotes in Table I.

Preliminary studies on the rates of reaction of azide ion with both chloroazido complexes were carried out. In these reactions an intense (ϵ >10,000) maximum grows at 295 nm. The reaction rates increase with the azide concentration and are independent of the platinum(II) concentration. The rates of these reactions are very slow. The products of the reactions are not known. However, there is evidence to suggest that the replacement of the remaining chloride ion by azide may not be occurring.

If reaction 4 (or the reaction of the corresponding ethylenediamine complex) is to occur by a platinum(II)-catalyzed mechanism, azide ion must function as the bridging group. The fact that solutions of *trans*-$Pt(NH_3)_4ClN_3^{2+}$ (or *trans*-$Pt(en)_2ClN_3^{2+}$) react very much more slowly in azide ion solutions than does *trans*-$Pt(NH_3)_4Cl_2^{2+}$ is proof that azide ion is a much poorer bridging group than chloride ion in platinum(II)-catalyzed reactions of platinum(IV) complexes. Moreover the slowness of the reaction and the absence of a rate dependence on $Pt(NH_3)_4^{2+}$ suggests that azide ion is totally ineffective as a bridging group for two-electron redox processes. On the basis of the known ability of azide as an entering group and of chloride ion as a leaving group, reaction 4 should occur at an appreciable rate if azide ion were at all effective in bridging.

$$\textit{trans}\text{-}Pt(NH_3)_4ClN_3^{2+} + N_3^- \rightarrow \textit{trans}\text{-}Pt(NH_3)_4(N_3)_2^{2+} + Cl^- \qquad (4)$$

The fact that azide ion is such a poor bridging group for these reactions and thiocyanate ion is a good one supports our previous proposal that thiocyanate ion bridges through the sulfur atom, Pt^{IV}–S–Pt^{II}. It seems unlikely that thiocyanate forms Pt^{IV}–SCN–Pt^{II} bridges along the reaction coordinate. Studies on one-electron inner-sphere redox reactions of light transition elements demonstrate that thiocyanate ion can serve as a triatomic bridge between redox centers,[5] for example, Cr^{III}–NCS–Cr^{II}. In such reactions thiocyanate ion is a poorer bridging group than azide ion when the reducing agent is bound to sulfur in the activated complex. It is the better bridging group when the reducing agent is bound to nitrogen. This has been explained in terms of the greater stability of N-bonded thiocyanate complexes of these light transition metals. In platinum chemistry, N-bonded thiocyanate is known only in a case in which NCS forms a triatomic bridge between two platinum(II) atoms.[6] On the basis of the generally accepted soft nature of this metal it seems certain that the sulfur-bonded complexes are the more stable. Therefore if azide ion and thiocyanate ion form triatomic bridges in platinum(II)-catalyzed platinium(IV) reactions, one would predict that azide should be a better bridging group than S-bonded thiocyanate. This is not the case.

The mechanism for platinum(II)-catalyzed reactions can be visualized as a nucleophilic substitution reaction in which a lone pair of electrons on the platinum(II) catalyst attacks the bridging atom (or group) and displaces the platinum atom which had been platinum(IV). The bridging ability of a group would then correlate with its susceptibility to nucleophilic attack. An oxygen, nitrogen, or fluorine atom would be expected to be ineffective. Triatomic groups such as N_3^- or NCS^- do not contain the correct conjugation to permit such a displacement. Sulfur, chlorine, and other heavy atoms have vacant d orbitals which can accept an extra electron pair from a nucleophile (or reducing agent); the light atoms could react only in a concerted process.

Comparison of the data for reaction 1 with those in the literature[2] indicates that azide ion as an entering ligand reacts several times faster than chloride ion (at 25° and $\mu = 0.015$, $k_3 = 6.5\ M^{-2}\ sec^{-1}$) and three-tenths as fast as bromide ion ($k_3 = 108\ M^{-2}\ sec^{-1}$ at 25° and $\mu = 0.20$).

Preliminary studies on the reverse of reaction 2 indicate that it is catalyzed by $Pt(en)_2^{2+}$ and has a first-order dependence on chloride ion (at 25° and $\mu = 0.80$, $k_3 = 0.065\ M^{-2}\ sec^{-1}$). The rate constant for $Pt(en)_2^{2+}$-catalyzed chloride exchange in *trans*-$Pt(en)_2Cl_2^{2+}$ was 15 $M^{-2}\ sec^{-1}$ (at 25° and $\mu = 0.02$). Azide ion is therefore displaced much more slowly than the halides previously studied. Their relative rates as leaving groups in *trans*-$Pt(NH_3)_4X_2^{2+}$ systems are $Br^- > SCN^- > Cl > I^-$ (11:4.4:3.8:1). The rate constants for reaction 2 permit the calculation of an equilibrium constant of 2.0×10^3 at 25°.

Experimental Section

Preparation of Compounds. Potassium tetrachloroplatinate,[7] $[Pt(NH_3)_4]Cl_2$,[8] $[Pt(NH_3)_4](ClO_4)_2$,[9] *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$,[9] *trans*-$[Pt(NH_3)_4Cl_2](NO_3)_2$,[9] $[Pt(en)_2]Cl_2$,[10] and *trans*-$[Pt(en)_2Cl_2]Cl_2$[10] were all prepared by published procedures.

***trans*-Azidochlorotetraammineplatinum(IV) Chloride.** One-half gram (1.23 mmol) of *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$ was suspended in 200 ml of a solution containing 0.023 g (0.068 mmol) of $[Pt(NH_3)_4]Cl_2$, 0.162 g (2.5 mmol) of NaN_3, and 5.00 ml of 0.234 *M* $HClO_4$ (1.17 mmol). The suspension stood in a dark locker for 4 days at about 22° with occasional stirring. After 3 days the $[Pt(NH_3)_4Cl_2]Cl_2$ had all dissolved. The solution was evaporated under vacuum at temperatures below 35° to a volume of 25 ml. Two milliliters of concentrated HCl was added to the ice-cold solution to precipitate the lemon yellow powder. The product was washed with 2 *M* HCl and 95% ethanol and dried at 50° under vacuum (0.387 g, 73% yield). The product is quite soluble in water. It can be dried to the anhydrous form at 50° under vacuum but rapidly picks up water from the atmosphere. The infrared spectrum of a Nujol mull of the complex has a strong peak at 2045 cm^{-1}. Anal. Calcd for $[Pt(NH_3)_4ClN_3]Cl_2 \cdot H_2O$: Pt, 45.4; N, 22.8; Cl, 24.8; H_2O, 4.2. Found: Pt, 45.9; N, 22.6; Cl, 26.4; H_2O, 2.6.

***trans*-Azidochlorobis(ethylenediamine)platinum(IV) Chloride.** Eight-tenths gram (1.68 mmol) of *trans*-$[Pt(en)_2Cl_2]Cl_2 \cdot H_2O$ and 0.003 g (0.008 mmol) of $[Pt(en)_2]Cl_2$ were dissolved in 13 ml of water. To this was added 25 ml of 0.50 *M* HN_3 (12.5 mmol) and 8.0 ml of 0.21 *M* LiOH (1.68 mmol). After 20 hr at 22° the excess HN_3 was extracted with three 45-ml portions of diethyl ether. The reaction solution was evaporated to 5 ml under vacuum. (The temperature was less than 35°.) Twenty milliliters of cold ethanol (100%) was added and lemon yellow crystals slowly formed. The product was washed with ethanol and ether and dried at 50° under vacuum (0.596 g, 73% yield). The product is very water soluble and the anhydrous product rapidly picks up water from the atmosphere. The infrared spectrum of the complex has a strong peak at 2040 cm^{-1}. Anal. Calcd for $[Pt(C_2H_8N_2)_2ClN_3]Cl_2 \cdot H_2O$: Pt, 40.5; C, 9.97; H, 3.77; N, 20.4; Cl, 22.1. Found: Pt, 40.5; C, 9.88; H, 3.79; N, 20.4; Cl, 22.0.

Other chemicals used in this study were reagent grade. Platinum analyses were done by ignition. Other analyses were done by Atlantic Microlab, Inc.

Kinetic Measurements. Kinetics were followed spectrophotometrically on a Beckman DU spectrophotometer modified with a Gilford 220 absorbance indicator. The cell compartment was thermostated to within ±0.02°. The reactions were studied under pseudo-first-order conditions. Reaction solutions were prepared in normal room light, and no change in rate was observed when a darkened room was used. In many cases duplicate kinetic runs were carried out and average values are reported. Duplicate runs reproduced reasonably well with deviations seldom being greater than 10%. Infinite-time absorbances on kinetic solutions were consistent with those expected from the spectra of the reaction products.

Rate data were analyzed by a Gauss–Newton nonlinear least-squares fit to the equation $A = A_0 + (A_0 - A_\infty) \exp(-kt)$. Absorbance vs. time data covering 4 half-lives were in general used and the fit to the equation was in general within the uncertainty of the absorbance measurements.

Registry No. $[Pt(NH_3)_4ClN_3]Cl_2$, 54566-84-6; $[Pt(C_2H_8N_2)_2ClN_3]Cl_2$, 54566-85-7; *trans*-$Pt(NH_3)_4Cl_2^{2+}$, 16986-23-5; *trans*-$Pt(en)_2Cl_2^{2+}$, 29646-65-9; N_3^-, 14343-69-2.

References and Notes

(1) (a) NSF undergraduate research participant. (b) Abstracted in part from the Ph.D. thesis of W.L.D.

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Infrared Spectra and Normal-Coordinate Analysis of 1,2-Dithiolate Complexes with Nickel

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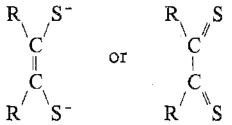
The infrared spectra of ten 1,2-dithiolate complexes of the type $[Ni(S_2C_2R_2)_2]^x$, where R is H, C_6H_5, CF_3, or CN and x is 0, 1−, or 2−, have been obtained. Nickel isotope substitution has been carried out to assign the Ni–S stretching modes. Normal-coordinate analyses have been made on all ten complexes to calculate the force constants as well as to give theoretical band assignments. The effects of changing the charge of the complex (x) and the substituent (R) on the stretching force constants have been discussed in terms of the Hückel MO theory.

Introduction

Metal complexes of 1,2-dithiolates or dithienes have been of great interest to inorganic chemists mainly because of their redox properties.[1,2] The oxidation state of the metal in dithienes is difficult to determine empirically. For example, the formal oxidation state of the metal in $Ni(S_2C_2R_2)_2$ may be +4 or 0 depending upon whether the ligand is regarded as a dinegative ion or a neutral species



The situation is more complicated if we consider a series of complexes such as $Ni(S_2C_2R_2)_2$, $[Ni(S_2C_2R_2)_2]^-$, and $[Ni(S_2C_2R_2)_2]^{2-}$ which have different net charges but almost identical geometrical structures.[3] Thus, the study of electron distribution in metal dithienes has been of particular interest to physical inorganic chemists. In fact, EPR spectra,[4] electronic spectra,[5] and X-ray photoelectron spectra[6] have been studied, and semiempirical MO calculations[7] have been made on metal dithienes.

As for vibrational spectra, Schrauzer and Mayweg[7] assigned the high-frequency infrared spectra and noted that the C=C stretching band gives the largest shift to a higher frequency as the negative charge of the complex increases. Adams and Cornell[8] assigned the metal–sulfur stretching bands of dithiene complexes (R = H, CF_3) and noted a slight decrease in frequency as the negative charge of the complex increases. Lakshmi et al.[9] reported the results of normal-coordinate analysis on the 1:1 metal–ligand model of the $[Ni(S_2C_2(CN)_2)_2]^{2-}$ ion. This was followed by Siiman and Fresco,[10] who carried out normal-coordinate analyses on neutral dithiene complexes with nickel, palladium, and platinum. However, these previous investigations led to conflicting assignments. Furthermore, no systematic studies have been made on the effects of changing the charge of the complex (x) and the substituent (R) on the infrared spectra of the $[Ni(S_2C_2R_2)_2]^x$ type complexes. In this paper, we have prepared ten dithiene complexes where R is H, C_6H_5, CF_3, or CN and n is 0, 1−, or 2− and assigned their infrared spectra based on nickel isotope shifts[11] and normal-coordinate analysis. The effects of changing R and x have been expressed in terms of force constants. An attempt has been made to interpret the changes in force constants by combining the Hückel MO theory with Gordy's equation.

Table I. Analytical Data

	% Ni		
	Calcd	Found	Ref
$Ni(S_2C_2H_2)_2$	24.56	24.45	11
$N(C_2H_5)_4[Ni(S_2C_2H_2)_2]$	15.89	15.98	11
$Ni(S_2C_2(CF_3)_2)_2$	11.48	11.35	12
$N(C_2H_5)_4[Ni(S_2C_2(CF_3)_2)_2]$	9.15	9.28	12
$[N(C_2H_5)_4]_2[Ni(S_2C_2(CF_3)_2)_2]$	7.60	7.75	12
$Ni(S_2C_2(C_6H_5)_2)_2$	10.80	10.65	13
$N(C_2H_5)_4[Ni(S_2C_2(C_6H_5)_2)_2]$	8.71	8.62	12
$(N_2H_5)_2[Ni(S_2C_2(C_6H_5)_2)_2]$	9.63	9.42	13
$N(C_2H_5)_4[Ni(S_2C_2(CN)_2)_2]$	13.67	13.54	12
$[N(C_2H_5)_4]_2[Ni(S_2C_2(CN)_2)_2]$	10.49	10.32	14

Experimental Section

All the complexes were prepared by the literature method.[12-15] The references for preparation are given in Table I. It also gives the results of nickel analysis obtained by complexometric titration. The purity of these compounds was checked by comparing their physical properties (melting point, spectra, etc.) with published data. The complexes containing nickel isotopes were prepared on a milligram scale using ^{58}Ni (99.98% pure) and ^{62}Ni (99.02% pure) purchased from Oak Ridge National Laboratory. The purity of these isotopic compounds was checked by comparing their infrared spectra with published data.

The infrared spectra were recorded on a Beckman IR 12 (4000–250 cm^{-1}) or a Perkin-Elmer Model 457 (4000–300 cm^{-1}) in KBr pellets or as Nujol mulls and on a Hitachi Perkin-Elmer FIS-3 far-infrared spectrophotometer (400–50 cm^{-1}) as Nujol mulls sandwiched between

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