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Octahedral Nickel(II) Complexes of Some Cyclic Polyfunctional Thioethers

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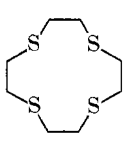
Three new macrocyclic ligands having only thioether donors have been synthesized. The nickel(II) tetrafluoroborate complexes have been prepared and characterized. All the complexes contain octahedral nickel(II) as the central metal ion and the physical properties are described and discussed in light of this result. Tetrafunctional macrocycles having only sulfur donors are too small to encompass the nickel(II) ion in square-planar chelation for ring sizes of 13 members or less. With nitrogen, the critical ring size occurs at one atom less, *i.e.*, 12 members. Such small tetrafunctional macrocycles form bridged complexes of the stoichiometry $Ni_2(MAC)_3{}^{2+}$. The electronic spectra of such dimers differ distinctly from those of complexes having threefold symmetry, *i.e.*, bis tridentate or tris bidentate.

Introduction

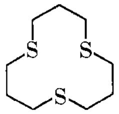
The study of metal complexes having only thioether chelates within the inner coordination sphere of a metal ion has only recently been undertaken.[1-6] The only example to date of a complex having the metal octahedrally substituted with six thioether groups is the case of the nickel(II) perchlorate complex of 2,5-dithiahexane (DTH).[1,3,5] We wish to report three new examples of such octahedrally coordinated nickel(II) ions and herein described their preparation and properties. These new complexes illustrate the relationships among macrocycle ring size, donor atom type, and mode of chelation.

Results and Discussion

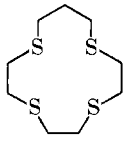
Three new ligands 1,4,7,10-tetrathiacyclotridecane (TTE, III), 1,4,7,10-tetrathiacyclodecane (TTC, I), and 1,5,9-trithiacyclododecane (TTD, II) were synthesized by procedures similar to those which have already been described[6] for other sulfur macrocycles. The macrocycles are all white sublimable solids having parent peaks in the mass spectra corresponding to their respective molecular weights. The nmr spectrum of TTD consists of a triplet of area 12 at τ 7.28 (CH_2's near sulfur) and a pentuplet of area 6 (CH_2's between CH_2's) at τ 8.08. A single sharp resonance at τ 7.24 is displayed by TTC (all CH_2 groups are alike), while TTE exhibits two singlets at τ 7.20 and 7.24 and a triplet at τ 7.34 with a combined area of 16 (CH_2's next to sulfur) and a pentuplet at τ 8.08 of area 2. This information coupled with the chemical analysis and the absence of S–H stretching bands in the ir spectra is enough to assign the structures uniquely as indicated above.



TTC
I



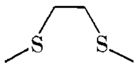
TTD
II



TTE
III

Complexation of the macrocycles is accomplished by means of the hexaacetic acid derivative of nickel(II) tetrafluoroborate.[6,7] In the case of TTC and TTE the same complexes are formed no matter what mole ratio of ligand to nickel(II) one employs.

The complexes all react with water which displaces the ligand intact. By the simple procedure of treating a known amount of complex with water, quantitatively filtering off the displaced macrocycle, and then precipitating the nickel(II) in the mother liquor with dimethylglyoxime, one can easily determine the ligand to metal ratio. In the case of the complexes of TTC and TTE the ratio was found to be 3:2 while the complex of TTD gave a ratio of 2:1. The complexes can therefore be formulated as $Ni_2(TTC)_3(BF_4)_4$, $Ni(TTD)_2(BF_4)_2$, and $Ni_2(TTE)_3(BF_4)_4$. The nickel(II) tetrafluoroborate complex of DTH (IV), made for comparison purposes, is formulated as $Ni(DTH)_3(BF_4)_2$ and is essentially identical with the perchlorate which has been prepared by others.[1,3,5]



DTH
IV

Conductivity studies performed in nitromethane are consistent with the formulations postulated above. Whereas the complexes of TTD and DTH exhibit the molar conductance values typical of 2:1 electrolytes, the complexes of TTC and TTE give much higher values (see Table I). Although there is no precedent for a 4:1 electrolyte in nitromethane solution, it is not unreasonable to expect values over 300 and this is what is found[8,9] for these "dimers."

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[1] R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

[2] H. C. E. Mannerskantz and G. Wilkinson, *ibid.*, 4454 (1962).

[3] R. L. Carlin and E. Weissberger, *Inorg. Chem.*, **3**, 611 (1964).

[4] F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4190 (1965); F. A. Cotton and R. A. Walton, *Inorg. Chem.*, **5**, 1802 (1966); M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966); F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967); R. A. Walton, *J. Chem. Soc.*, 1852 (1967).

[5] C. D. Flint and M. Goodgame, *ibid.*, *A*, 2178 (1968).

[6] W. Rosen and D. H. Busch, *Chem. Commun.*, 148 (1969); *J. Am. Chem. Soc.*, **91**, 4694 (1969).

[7] P. W. N. M. van Leeuwen and W. L. Groeneveld, *Rec. Trav. Chim.*, **87**, 86 (1968).

[8] A 3:1 electrolyte in nitromethane solution exhibits a molar conductivity in the range 230–260: D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **86**, 1331 (1964); J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).

[9] S. C. Cummings, Dissertation, The Ohio State University, 1968.

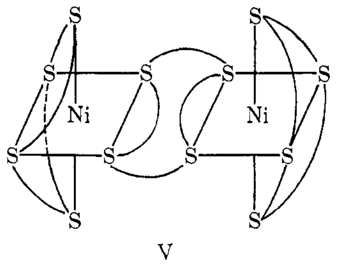
TABLE I

PHYSICAL PROPERTIES OF THE COMPLEXES $Ni_nL_m(BF_4)_p$

Ligand	n	m	p	μ_{eff}, BM[a]	Λ_M,[c] mho cm^2/mol	ν_{max}, cm^{-1} CH$_3$NO$_2$[d]	Solid	B,[e] cm^{-1}
TTE	2	3	4	3.07[b]	334	10,000 sh (~120)	10,000 sh	
						11,400 (156)	11,200 ν_1	907
						19,000 (238)	19,000 ν_2	
							28,200 ν_3	
TTC	2	3	4	3.06[b]	318	9,500 sh (139)	9,300 sh	
						10,500 (181)	10,400 ν_1	880
						17,200 (67)	17,400 ν_2	
							27,000 ν_3	
TTD	1	2	2	3.19	186	10,300 sh (~12)	10,200 sh	
						11,200 (18)	11,100 ν_1	713
						17,500 (31)	17,700 ν_2	
							26,300 ν_3	
DTH	1	3	2	3.15	182	10,000 sh (22)	9,700 sh	
						11,100 (37)	10,900 ν_1	747
						17,400 (33)	17,200 ν_2	
							26,700 ν_3	

[a] Obtained by both nmr and Faraday measurements. [b] μ_{eff} per nickel atom. [c] Solution is 10^{-3} M. [d] Molar extinction coefficient in parentheses. [e] A. B. P. Lever, *J. Chem. Educ.*, **45,** 711 (1968).

The infrared spectra of all the complexes display bands typical of ionic BF$_4$ while a ^{11}B nmr spectrum of a nitromethane solution of $Ni_2(TTE)_3(BF_4)_4$ exhibits one sharp resonance approximately 1.4 ppm downfield from $BF_3 \cdot O(C_2H_5)_2$. All the complexes exhibit behavior typical of high-spin nickel(II). They all have magnetic moments within the range 3.0–3.2 BM, whether in the solid state or in nitromethane solutions (Table I). This is the range within which most octahedral nickel(II) complexes fall and is in accord with the metal being octahedrally surrounded by six thioethers. A structure for the "dimer" cations is proposed below (V). It is drawn in analogy to that proposed for $Ni_2(trien)_3Cl_4 \cdot 2H_2O$.[10]



V

It is interesting to note at this point that when a macrocycle has four nitrogens as the donor atoms, a 13-membered ring is able to span the equatorial positions of a metal and coordinate with its four donor atoms in a square-planar array; whereas, with a 12-membered ring it is not able to do so and chelates in a folded manner.[11] When the donor atoms are all sulfurs, the 13-membered ring is unable to circumscribe the nickel(II) ion and chelate with its donors in a single plane. This confirms the expectation that the hole in the macrocycle is smaller when sulfur is the donor than when nitrogen is the donor.

The near-ir–visible spectra of the complexes are recorded in Table I and Figure 1. The solid-state and solution spectra are essentially identical with the exception that the spectra of nitromethane solutions could not be recorded below 400 mμ, due to solvent absorption, thus obscuring the highest energy d–d transition observable in the solid-state spectra. All spectra exhibit three major d–d transitions, ν_1, ν_2, and ν_3 (see Table I), as has already been noted for $Ni(DTH)_3(ClO_4)_2$. These transitions are assigned as follows: $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3).[12] There is a shoulder on the low-energy side of ν_1. This shoulder is most easily observed in solution (Figure 1) but can be detected in the solid-state spectra upon careful examination. The origin of this shoulder is not clear, but one can speculate that it may be a transition from the ground state to the lowest lying singlet state, *i.e.*, $^1E_g(D)$. Alternatively, it may be due to a ligand distortion of the field about the metal from regular octahedral, resulting in a splitting of the bands (the lowest energy band would be split to a greater extent than the others). Assignment of this low-energy shoulder remains uncertain.

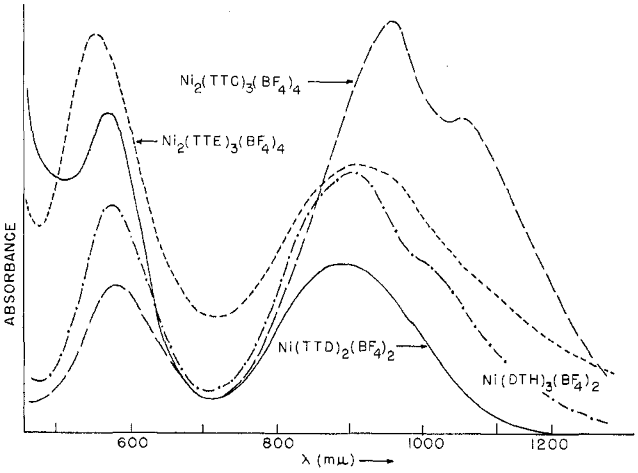


Figure 1.—The electronic spectra of the new complexes.

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(10) H. B. Jonassen and B. E. Douglas, *J. Am. Chem. Soc.*, **71,** 4094 (1949).

(11) D. A. House and N. F. Curtis, *ibid.*, **86,** 1331 (1964); J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5,** 1380 (1966).

(12) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **2,** 134 (1959).

From the spectra one can calculate Dq $(=\nu_1/10)$ for these complexes as being in the range 1040–1120 cm^{-1}. This is consistent with values for other thioether complexes.[6] The Racah parameter B can also be calculated[13] and values are given in Table I. The B values seem to classify the complexes into two groups. Those having two nickel atoms in the molecule have values in the neighborhood of 900 cm^{-1} while the complexes with only one nickel in the molecule have values at about 725 cm^{-1}. These two groups are similarly differentiated by the molar extinction coefficients of their absorption bands, which are higher for the former than the latter. The significance of these observations awaits the results of further work. Studies on these complexes are continuing in our laboratories.

Experimental Section

All chemicals used in this work were either prepared by the following procedures or obtained commercially. The nitromethane used was Spectrograde from Eastman Organic Chemicals which had been purified by well-known procedures.[14] All nmr spectra were recorded on a Varian A-60 spectrometer while infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer. Visible and near-ir spectra were recorded on a Cary 14 spectrophotometer either by using nitromethane solutions or by diffuse transmittance of Nujol mulls. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectral data were provided by Mr. Dick Weissenberger of the Department of Chemistry, The Ohio State University, using an MS-9 spectrometer. Conductivity measurements were obtained on 10^{-3} M nitromethane solutions in a standard 15-ml conductivity cell in conjunction with an Industrial Instruments conductivity bridge, Model RC 16B. Magnetic susceptibility measurements were made by both Faraday and nmr[15] techniques.

Preparation of 1,4,7,10-Tetrathiacyclotridecane (TTE).—In 500 ml of absolute ethanol under N_2 was dissolved 4.6 g (0.2 g-atom) of sodium metal. After the sodium had dissolved 22.8 g (0.1 mol) of 1,4,8,11-tetrathiaundecane[6] was added. This solution was then gently refluxed and 18.8 g (0.1 mol) of 1,2-dibromoethane was slowly and cautiously added. After this addition was complete, the mixture was refluxed an additional 5 hr and was then cooled. The solvent was removed and the resulting solid was dissolved in 300 ml of chloroform and 250 ml of water. The layers were separated and the chloroform layer was washed with 100 ml of water and dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered off and the chloroform was removed on a rotary evaporator. The solid that remained was recrystallized from an ethanol–chloroform mixture. The solid was then sublimed at 140° (5 mm) and recrystallized again; yield, 4.0 g (16%); mp 134–135 The infrared spectrum did not have an S–H stretch at 3.9 μ. The mass spectrum displayed a parent peak at m/e 254 (theory 254.5). The nmr spectrum displayed a singlet at τ 7.20, a singlet at τ 7.24, and a triplet at τ 7.34 (J = 7 cps) with a combined area of 16, and a pentuplet at τ 8.08 (J = 7 cps) of area 2. *Anal.* Calcd for $C_9H_{18}S_4$: C, 42.47; H, 7.13; S, 50.40. Found: C, 42.14; H, 7.31; S, 50.07.

Preparation of 1,4,7,10-Tetrathiadecane.—After 11.5 g (0.5 g-atom) of sodium metal had been dissolved in 750 ml of absolute ethanol, 23.5 g (0.25 mol) of 1,2-ethanedithiol was added. The resulting mixture was gently refluxed under N_2 and 40.25 g (0.5 mol) of 2-chloroethanol was cautiously added. The mixture was stirred and refluxed overnight; it was then cooled and filtered, and the solvent was removed leaving a solid. To this solid was added 110 ml of concentrated HCl and 37 g of thiourea. This mixture was gently refluxed for 4 hr and then was cooled. At this point, 74 g of KOH in 400 ml of water was very cautiously added. The mixture was refluxed an additional 3 hr. After cooling, the two-layered system was extracted with 300 ml of chloroform. The chloroform layer was dried over anhydrous $MgSO_4$ and filtered, and the chloroform was removed leaving a thick liquid which was distilled. After a small forerun, the product was collected, bp 160–162° (0.5 mm); yield, 19.0 g (35.5%).

Preparation of 1,4,7,10-Tetrathiacyclododecane (TTC).—In 750 ml of absolute ethanol was dissolved 3.7 g (0.16 g-atom) of sodium metal under N_2 and this was followed by 18.0 g (0.08 mol) of 1,4,7,10-tetrathiadecane. When the solution became homogeneous 15.0 g (0.08 mol) of 1,2-dibromoethane was cautiously added to the refluxing mixture. The mixture was refluxed for 12 hr after which it was filtered hot and allowed to cool. The solvent was removed from the cooled filtrate and the solid that resulted was Soxhlet extracted with ether for 24 hr. The ether was removed and the solid that remained was then sublimed at 140° (0.5 mm). The sublimed solid was recrystallized from an ethanol–chloroform mixture; mp 215–217° (sublimes between 170 and 215°); yield, 0.8 g (4%). The infrared spectrum did not have a peak at 3.9 μ. The mass spectrum had a parent peak at m/e 240 (theory 240.5). The nmr spectrum had a single sharp resonance at τ 7.24. *Anal.* Calcd for $C_8H_{16}S_4$: C, 39.96; H, 6.71; S, 53.33. Found: C, 40.12; H, 6.58; S, 53.01.

Preparation of 1,5,9-Trithianonane.—In 400 ml of ethanol was dissolved 30.0 g (0.125 mol) of $Na_2S \cdot 9H_2O$ and 34.8 g (0.25 mol) of 3-bromo-1-propanol was then added. This mixture was refluxed for 12 hr, cooled, and filtered, and the ethanol was removed. To the liquid that remained was added 17.5 g (0.25 mol) of thiourea and 60 ml of concentrated HCl, and this mixture was refluxed for 8 hr. After cooling, 37 g of KOH in 200 ml of water was cautiously added and the mixture was cooled and extracted with 150 ml of chloroform. The $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed leaving a mobile liquid. This liquid was distilled, bp 118–120° (0.5 mm); yield, 3.0 g (13%).

Preparation of 1,5,9-Trithiacyclododecane (TTD).—In 800 ml of absolute ethanol under N_2 was dissolved 2.7 g (0.12 g-atom) of sodium metal and to this stirring mixture was then added 10.5 g (0.06 mol) of 1,5,9-trithianonane. The mixture was refluxed and 11.6 g (0.06 mol) of 1,3-dibromopropane was slowly added. This mixture was refluxed for 12 hr. The solution was cooled and filtered, and the solvent was removed leaving a liquid. Upon distillation a solid codistilled with a liquid, and the solid was filtered off and washed with a small amount of cold n-hexane. The solid proved to be the desired product, mp 87–88°; yield, 0.4 g (3%). The infrared spectrum showed no band at 3.9 μ. The mass spectrum had a parent peak at m/e 222 (theory 222.5). The nmr spectrum displayed a triplet at τ 7.28 (J = 6 cps) of area 12 and a pentuplet at τ 8.08 (J = 6 cps) of area 6. *Anal.* Calcd for $C_9H_{18}S_3$: C, 48.60; H, 8.16; S, 43.24. Found: C, 48.39; H, 8.32; S, 43.76.

Preparation of $Ni_2(TTE)_3(BF_4)_4$.—To 2.49 g (7.30 mmol) of $Ni(BF_4) \cdot 6H_2O$ in 60 ml of dry nitromethane was added 4.56 g (45 mmol) of acetic anhydride. The mixture was stirred until the solid had dissolved and then 2.79 g (10.95 mmol) of 1,4,7,10-tetrathiocyclotridecane was added all at once. The color of the solution changed immediately from green to violet, and after stirring for 0.5 hr the mixture was filtered into 400 ml of anhydrous ether and the oil was allowed to separate. The colorless solution above the oil was decanted and the oil was dried *in vacuo* to a glass. The glass was placed in a Soxhlet-extraction thimble and was extracted with 500 ml of dry acetone for a few hours. The volume of the resulting blue solution was reduced to approximately 200 ml, and it was then placed in the refrigerator to precipitate any excess ligand present. After filtering this cold solution the complex was precipitated with anhydrous ether and the violet complex was filtered and washed thoroughly with ether. The solid was then dried *in vacuo*; yield, 3.6 g (81%). *Anal.* Calcd

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(13) A. B. P. Lever, *J. Chem. Educ.*, **45**, 711 (1968).

(14) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardin, *J. Am. Chem. Soc.*, **86**, 1039 (1964).

(15) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

for $Ni_2C_{27}H_{54}S_{12}B_4F_{16}$: C, 26.41; H, 4.43; S, 31.33; Ni, 9.56. Found: C, 26.58; H, 4.35; S, 31.19; Ni, 9.92.

Preparation of $Ni_2(TTC)_3(BF_4)_4$.—To 0.43 g (1.39 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ in 10 ml of anhydrous nitromethane was added 0.87 g (8.55 mmol) of acetic anhydride. The mixture was stirred until the solid had dissolved, and then 0.50 g (2.08 mmol) of 1,4,7,10-tetrathiacyclododecane was added all at once. The solution immediately changed from green to blue. The mixture was allowed to stir for 0.5 hr and was then filtered into 100 ml of anhydrous ether. The blue precipitate was filtered, washed with ether, and dried *in vacuo*. This blue precipitate was placed in a Soxhlet extraction thimble and was extracted with 100 ml of dry acetone for a few hours. The volume of the resulting blue solution was reduced to approximately one-fourth and the complex was then precipitated with anhydrous ether. The blue solid was filtered, washed with ether, and dried *in vacuo;* yield, 0.71 g (84%). *Anal.* Calcd for $Ni_2C_{24}H_{48}S_{12}B_4F_{16}$: C, 24.30; H, 4.08; S, 32.44; Ni, 9.90. Found: C, 24.32; H, 3.74; S, 32.42; Ni, 9.99.

Preparation of $Ni(TTD)_2(BF_4)_2$.—To 245 mg (0.72 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ in 10 ml of dry nitromethane was added 440 mg of acetic anhydride. After the solid had dissolved 317 mg (1.43 mmol) of 1,5,9-trithiacyclododecane was added with stirring and the green color immediately turned to a red-brown. After stirring for 20 min the solution was filtered into 75 ml of anhydrous ether, and the precipitate which formed was filtered, washed with 100 ml of ether, and dried *in vacuo;* yield, 0.31 g (69%). *Anal.* Calcd for $NiC_{18}H_{36}S_6B_2F_8$: C, 31.93; H, 5.36; S, 28.41; Ni, 8.67. Found: C, 31.27; H, 4.98; S, 28.76; Ni, 8.28.

Preparation of $Ni(DTH)_3(BF_4)_2$.—This compound was prepared in an analogous way to that above in 85% yield, using the hexaacetic acid derivative of $Ni(BF_4)_2$ and 2,5-dithiahexane in nitromethane.

Acknowledgment.—We are indebted to the National Institutes of Health of the U. S. Public Health Service for support under Grant GM-10040 and Fellowship No. 5 FO2GM 28951-02. We also wish to thank Mr. Kent Travis for technical assistance and Dr. Howard D. Johnson, II, for running the ^{11}B nmr spectrum for us.

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Solvent Effects in Platinum(II)-Catalyzed Substitution Reactions of Platinum(IV) Complexes

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The rate of replacement of chloride ions in *trans*-$Pt(en)(NO_2)_2Cl_2$ and *trans*-$Pt(dien)NH_3Cl_2^{2+}$ by bromide ions has been studied in water, water–methanol, and water–dioxane solutions. The reaction rates are quite sensitive to solvent composition and increase in the case of the cationic complex and decrease in the case of $Pt(en)(NO_2)_2Cl_2$ as the solvent polarity is lowered. The reactions are catalyzed by the appropriate platinum(II) complex and a first-order rate dependence on catalyst was observed in all solvents used.

Introduction

A probable mechanism for a wide variety of substitution reactions of platinum(IV) complexes is presented in eq 1–3.[1] The mechanism is illustrated in terms

$$\mathrm{Pt(II)} + \mathrm{Br}^- \rightleftharpoons \mathrm{Pt(II)}\cdots\mathrm{Br}^- \qquad (1)$$

$$\mathrm{Cl{-}Pt^{IV}{-}Cl} + \mathrm{Pt(II)}\cdots\mathrm{Br}^- \longrightarrow \mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Br}^- \qquad (2)$$

$$\mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Cl}\cdots\mathrm{Pt}\cdots\mathrm{Br}^- \longrightarrow \mathrm{Cl}^- + \mathrm{Pt(II)} + \mathrm{Cl{-}Pt^{IV}{-}Br} \qquad (3)$$

of the reactions reported in this paper with the ligands in the platinum(II) complex and those *cis* to the reactive *trans*-dihalo axis of the platinum(IV) complex omitted for the sake of simplicity and generality.

No direct evidence for the intermediate postulated in step 1 has been presented for ammonia complexes. However, such species are known in both solution and solid states when the ligands in the square plane are good π acceptors.[2-4] It is possible that there are other preequilibria, for example, one involving association of the platinum(IV) and platinum(II) complexes. Since a variety of kinetic work in aqueous solution has failed to provide direct evidence for intermediates in reactions of ammonia complexes, it seemed appropriate to look for evidence in less polar solutions. If an appreciable fraction of the platinum(II) catalyst became associated with either bromide ion or the platinum(IV) complex, the rate law would deviate from the simple third-order behavior normally observed.

Although some rate studies on substitution reactions of platinum(IV) complexes have been made in nonaqueous solution (for example see ref 4), we are not aware of any in which a given reaction was studied in more than one solvent. This article provides such information on solvent effects in platinum(II)-catalyzed reactions of platinum(IV) complexes.

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[1] S. G. Bailey and R. C. Johnson, *Inorg. Chem.*, **8**, 2596 (1969), and references therein.

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[3] A. D. Westland, *ibid.*, 3060 (1965).

[4] A. Peloso and G. Dolcetti, *Coord. Chem. Rev.*, **1**, 100 (1966).