it to be dimeric. Such determination was not possible for the (N-P) complex due to its lower solubility.

The reaction of 8-aminoquinoline with $[Rh(CO)_2Cl_2]^-$ is remarkable. The yellow color of the ethanolic solution of the anion changes immediately upon mixing to orange-yellow. After 10 min of gentle reflux, a yellow precipitate separated. After about 1 h of reflux, the yellow precipitate started to disappear giving way to the formation of a greenish solution followed by the precipitation of a greenish solid. At the end of 2 h of reflux, the greenish precipitate completely disappeared to give a pale yellow product which did not show any changes after 48 h of reflux. All of these compounds did not contain any carbonyl groups as shown by their identical infrared spectra. The formation of the pale yellow product was accompanied with the oxidation of Rh(I) to Rh(III). Moreover, the properties of the product are different from those of the complex isolated from the direct reaction of Rh(III) with (N-N). The infrared spectrum shows $\nu_{N-H}$ bands at 3350 and 3120 cm$^{-1}$, indicative of free and coordinated $NH_2$, respectively (in addition to $\nu_{OH}$ at 3595 cm$^{-1}$). The complex is therefore formulated as $Rh(N\text{-}N)_2Cl_3{\cdot}H_2O$, with one monodentate ligand and one bidentate (N-N) ligand. The water molecule is most probably held by the uncoordinated $NH_2$ group. However, heating the compound to 150 °C did not result in any apparent loss of water or in any loss of weight.

**Reactions of $Pd(C_6H_5CN)_2Cl_2$.** The three ligands behaved in an identical manner in their reactions with $Pd(C_6H_5CN)_2Cl_2$ affording $Pd(N\text{-}As)Cl_2$, $Pd(N\text{-}P)Cl_2$, and $P(N\text{-}N)Cl_2$. The last complex is identical with an authentic compound prepared by a literature procedure.[11] A different complex of Pd(II), namely, $Pd(N\text{-}N)_2Cl_2$, has also been reported.[2b] All of the complexes of Pd(II) synthesized in our work are nonelectrolytes in the proper solvents. They are presumably square planar. Two $\nu_{Pd-Cl}$'s were observed in the IR spectrum of each of the complexes, consistent with the cis arrangement of the Cl ligands.

**Reactions of $K_2PtCl_4$.** Platinum(II) behaved typically with all three ligands yielding the complexes $Pt(N\text{-}As)Cl_2$, $Pt(N\text{-}P)Cl_2$, and $Pt(N\text{-}N)Cl_2$. The complexes are nonelectrolytes in the proper solvent. The (N-N) complex shows a $\nu_{N-H}$ at 3120 cm$^{-1}$ in its infrared spectrum, indicating a coordinated $NH_2$ group. The complexes are presumably square planar. The IR spectra show two $\nu_{Pt-Cl}$ in each complex corresponding to two Cl ligands in a cis arrangement.

The stabilization of unusual oxidation states by the (N-P) and (N-As) ligands may provide a means of synthesizing some complexes that may be potential catalysts.

**Registry No.** N-As, 34943-65-2; N-P, 28225-52-7; N-N, 578-66-5; $Ru(N\text{-}As)(Me_2SO)_2Cl_2$, 69501-69-5; $Ru(N\text{-}N)(Me_2SO)_2Cl_2$, 69501-70-8; $Ru_2(Me_2SO)_5Cl_4$, 69501-71-9; $[Rh(N\text{-}As)Cl_3]_2$, 69501-95-7; $Rh(N\text{-}P)Cl_2$, 69501-96-8; $[Rh(N\text{-}N)_2Cl_2]Cl$, 69596-92-5; $[Rh(N\text{-}As)(CO)Cl_2]_2$, 69501-77-5; $[Rh(N\text{-}P)(CO)Cl_2]_2$, 69501-78-6; $Pd(N\text{-}As)Cl_2$, 69501-79-7; $Pd(N\text{-}P)Cl_2$, 69501-80-0; $Pd(N\text{-}N)Cl_2$, 15038-39-8; $Pt(N\text{-}As)Cl_2$, 69501-81-1; $Pt(N\text{-}P)Cl_2$, 69501-82-2; $Pt(N\text{-}N)Cl_2$, 64828-04-2; $Ru(Me_2SO)_4Cl_2$, 11070-19-2; $Rh(N\text{-}N)_2Cl_3$, 69508-44-7; $[Rh(CO)_2Cl_2]^-$, 15550-00-2; $Pd(C_6H_5CN)_2Cl_2$, 14220-64-5; $K_2PtCl_4$, 10025-99-7.

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# Monomeric Complexes of Palladium(II) and Platinum(II) with a Series of Open-Chain Tetrathioether Ligands Prepared from Complexes of Weak Donor Ligands

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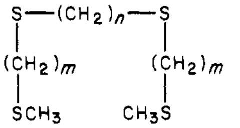
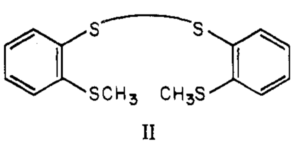
We have been interested for some time in the coordination chemistry of thioether ligands and have previously reported that the open-chain tetrathioethers I and II are unable to replace all the halide ligands around palladium(II) and platinum(II) to form monomeric complexes $[M(S_4)]X_2$ in which $S_4$ is I or II. Instead these ligands form complexes $[M_2(S_4)X_4]$, which are probably polymeric and which have the metal ion surrounded by two sulfur atoms and two halide ions.[3-5] It was of interest to determine whether our failure to prepare monomeric complexes with all four sulfur donors of a given ligand coordinated was due to either steric or electronic factors inherent in the ligand or merely due to the inability of the ligands to compete successfully with halide ligands. Our previous interest in solvento complexes[6,7] suggested that these would provide useful halide-free starting materials with which to distinguish these two alternatives. Accordingly, we report the reaction of $[M(MeCN)_4](ClO_4)_2$ (M = Pd, Pt) with a series of tetrathioether ligands I and II.



I

| | |
|---|---|
| $n = m = 2$ | 2,2,2 |
| $n = m = 3$ | 2,3,2 |
| $n = 2, m = 3$ | 3,2,3 |
| $n = 3, m = 2$ | 3,3,3 |



II

| | |
|---|---|
| ⌒ = $(CH_2)_2$ | bme |
| ⌒ = $(CH_2)_3$ | bmp |
| ⌒ = $(CH_2)_4$ | bmb |
| ⌒ = *cis*-CH=CH– | bmv |

## Experimental Section

The tetrathioether ligands were prepared as described previously.[3,4] All solvents were used as purchased. The silver perchlorate was dried at 78 °C for 12 h at $10^{-3}$ torr and stored in a desiccator over $P_2O_5$.

**$[M(CH_3CN)_2Cl_2]$ (M = Pd, Pt).** The appropriate $MCl_2$ (2 g) was stirred in refluxing acetonitrile until a clear solution was obtained (about 1 h). This was filtered hot and reduced to small volume on a rotary evaporator, and then the product was filtered off, washed with ether, and dried in vacuo. Yields were 85–90%. Anal. Calcd for $C_4H_6Cl_2N_2Pd$: C, 18.5; H, 2.3; N, 10.8. Found: C, 18.4; H, 2.4; N, 11.0. Calcd for $C_4H_6Cl_2N_2Pt$: C, 13.8; H, 1.7; N, 8.0. Found: C, 13.9; H, 1.9; N, 8.0.

**Palladium Complexes.** The palladium complexes were prepared by the following general procedure. $[Pd(CH_3CN)_2Cl_2]$ (1 mmol, 0.259 g) was dissolved in warm acetonitrile (20 cm$^3$), $[AgClO_4]$ (2 mmol, 0.415 g) dissolved in acetonitrile (5 cm$^3$) was added, and the mixture was stirred at room temperature for 1 h and then the silver chloride precipitate was filtered off. (Attempts to isolate $[Pd(CH_3CN)_4](ClO_4)_2$ by evaporation or precipitation gave a yellow solid which

**Table I.** $[M(S_4)](ClO_4)_2$ Complexes

| complex | color | analyses,[a] % |  |  | conductivities[b] |  | electronic spectra[c] |
|---|---|---|---|---|---|---|---|
|  |  | C | H | N | $B^d$ | $\Lambda_M{}^e$ | $\lambda_{max}$, nm ($\epsilon_{mol}$)[f] |
| $[Pd(2,2,2)](ClO_4)_2$ | yellow | 17.6 (17.9) | 3.3 (3.7) |  | [g] | [g] | [g] |
| $[Pd(2,3,2)](ClO_4)_2$ | yellow | 19.3 (19.5) | 3.5 (3.4) |  | 424.8 | 171.6 | 280.0 (17 800), 318.0 (5400, sh) |
| $[Pd(3,2,3)](ClO_4)_2$ | yellow | 20.8 (20.5) | 3.9 (4.1) |  | 476.7 | 175.2 | 277.2 (17 800), 340.0 (7100) |
| $[Pd(3,3,3)](ClO_4)_2$ | yellow | 22.4 (22.7) | 4.1 (3.9) |  | 422.5 | 169.0 | 287.9 (16 600), 332.0 (5800, sh) |
| $[Pd(bme)](ClO_4)_2$ | yellow | 29.8 (28.6) | 2.8 (2.3) |  | 323.3 | 148.8 | 274.4 (6950), 292.0 (4400, sh), 332.3 (1000, sh) |
| $[Pd(bmp)](ClO_4)_2$ | yellow | 31.1 (31.5) | 3.1 (3.4) |  | 466.0 | 179.6 | 274.5 (9600), 291.8 (5520, sh), 330.0 (2100, sh) |
| $[Pd(bmb)](ClO_4)_2$ | yellow | 32.2 (32.1) | 3.3 (3.6) |  | 420.0 | 162.4 | 275.0 (7600), 292.0 (4920, sh), 328.2 (1300, sh) |
| $[Pt(2,2,2)](ClO_4)_2$ | white | 15.1 (15.4) | 2.9 (3.0) |  | 399.2 | 155.6 | 226.4 (10 800), 260.8 (3600, sh), 315.2 (1040, sh) |
| $[Pt(2,3,2)](ClO_4)_2$ | white | 16.6 (16.7) | 3.1 (3.3) |  | 446.6 | 166.6 | 228.4 (17 400), 257.6 (5900, sh), 313.6 (880) |
| $[Pt(3,2,3)](ClO_4)_2 \cdot CH_3NO_2$ | white | 18.2 (18.1) | 3.5 (3.4) | 1.9 (1.9) | 437.6 | 170.8 | 224.8 (13 700), 276.8 (4060), 312.0 (1060, sh) |
| $[Pt(3,3,3)](ClO_4)_2 \cdot CH_3NO_2$ | white | 19.5 (19.6) | 3.7 (3.6) | 1.8 (1.6) | 430.8 | 170.8 | 232.0 (13 000), 272.0 (3360, sh), 317.6 (630, sh) |
| $[Pt(bme)](ClO_4)_2$ | yellow | 26.3 (26.8) | 2.5 (2.8) |  | 341.1 | 132.4 | 230.4 (19 400), 256.0 (13 400, sh), 328.0 (1800, sh) |
| $[Pt(bmp)](ClO_4)_2$ | white | 27.4 (27.6) | 2.7 (2.8) |  | 402.0 | 184.4 | 229.6 (18 800), 267.2 (5000, sh), 312.0 (1370, sh) |
| $[Pt(bmb)](ClO_4)_2$ | white | 28.4 (28.3) | 2.9 (3.3) |  | 426.3 | 179.2 | 228.0 (18 300), 262.4 (5800, sh), 321.6 (1320, sh) |

[a] Calcd (Found). [b] In nitromethane. [c] In acetonitrile. [d] See eq 1; $B$ is in $\Omega^{-1}$ $L^{1/2}$ equiv$^{-1/2}$. [e] Molar conductance values ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) for $10^{-3}$ M solutions. [f] Absorption coefficients of unresolved bands (dm$^3$ mol$^{-1}$ cm$^{-1}$). [g] Insufficient solubility in appropriate solvents for determination.

decomposed after several hours. This complex has been isolated from palladium metal and acetonitrile by using $[NOBF_4]$ as oxidant;[8] however, we have found that our method gives a suitable intermediate in solution.) To the filtrate was added the appropriate tetrathioether ligand (1 mmol) in acetonitrile (5 cm$^3$) with stirring. After 1 h more the reaction mixture was filtered to remove a small amount of solid, the resulting filtrate was evaporated to dryness, extracted with nitromethane (20 cm$^3$), filtered, and evaporated to small volume, and then the complex was precipitated with either acetone or diethyl ether and dried in vacuo. Yields were 60–70%.

**Platinum Complexes.** The platinum complexes were prepared in a similar manner. Here the halide abstraction by the silver ion required 2 h in refluxing acetonitrile until the original yellow solution of $[Pt(CH_3CN)_2Cl_2]$ had turned colorless. The $[Pt(CH_3CN)_4](ClO_4)_2$ can be isolated from this reaction;[9] however, we used it in solution as for the palladium complexes. The final precipitation of the complexes from the nitromethane extraction could not be achieved with acetone but required diethyl ether. Yields were 65–75%.

**Physical Measurements.** Infrared spectra were recorded in the region 4000–200 cm$^{-1}$ as mulls in both Nujol and hexachlorobutadiene on the Perkin-Elmer 577 grating spectrometer, NMR spectra were recorded on the Perkin-Elmer R32 90-MHz spectrometer in $CD_3NO_2$ or dimethyl-$d_6$ sulfoxide with tetramethylsilane as internal standard, and electronic spectra were recorded on the Pye-Unicam SP 1700 spectrometer as $10^{-3}$ M or $10^{-4}$ M solutions in acetonitrile. Conductivities were measured over the range $10^{-2}$–$10^{-5}$ equivalent solutions in nitromethane[10] on a Universal Wayne-Kerr conductivity bridge between platinum electrodes. Microanalyses were performed by the microanalytical laboratories at the chemistry departments of the University of Kent, Canterbury, and University College, London.

## Results and Discussion

The thioether ligands I and II easily replace the weakly bound acetonitrile ligands in $[M(CH_3CN)_4](ClO_4)_2$ to form the $[M(S_4)](ClO_4)_2$ complexes shown in Table I, which have been characterized on the basis of analytical, spectroscopic, and conductance data. The electronic spectra of the $[M(S_4)](ClO_4)_2$ complexes (Table I) in the region 310–500 nm are indicative of square-planar coordination, not five-coordination, since there are no bands at wavelengths above 370 nm.[11] Infrared spectra in the 400–200-cm$^{-1}$ region show the absence of metal–halogen associated bands. The several weak absorptions observed in the region are probably associated principally with the metal–sulfur bonds. All the complexes show a strong broad unsplit band at about 1080 cm$^{-1}$ ($\nu_3$) and a sharp medium-strength band at about 620 cm$^{-1}$ ($\nu_4$) due to uncoordinated perchlorate.[12] No absorptions are present at about 2300 cm$^{-1}$ showing the complete removal of the previously coordinated acetonitrile.

Three structures are possible for a complex of empirical formula $[M(S_4)](ClO_4)_2$ in which the anions are uncoordinated and the metal ion is square planar: a monomer (III), a dimer (IV), or a polymer (V). Since the complexes are reasonably soluble in polar solvents, structure V is very unlikely. The molar conductivities of the complexes cannot differentiate between III and IV, but the concentration dependence of the equivalent conductivities can. Thus using the Debye-Hückel equation (eq 1), where $B$ is a constant dependent on ion type,

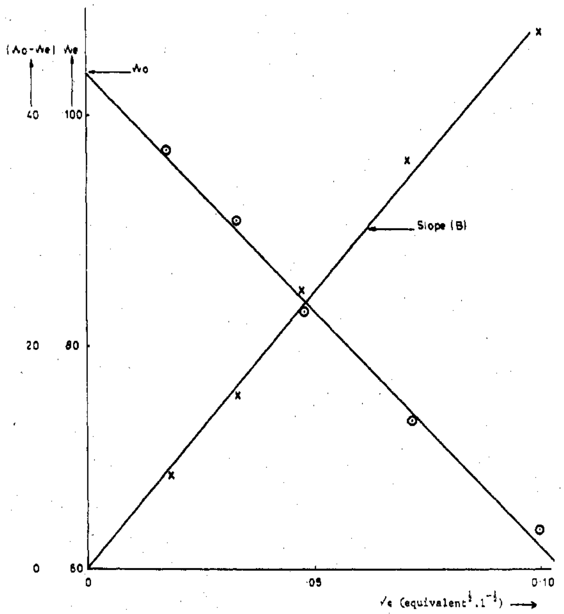
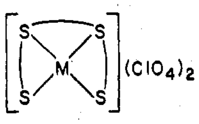
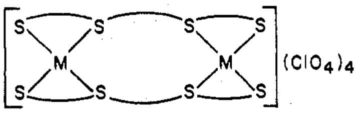


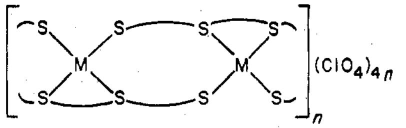
**Figure 1.** Conductivity dilution study of $[Pt(3,3,3)](ClO_4)_2$ in nitromethane.



III



IV



V

$$\Lambda_e = \Lambda_0 - Bc^{1/2} \qquad (1)$$

$\Lambda_0$ is the conductance at infinite dilution, and $\Lambda_e$ is the conductance at an equivalent concentration $c$, we may dif-

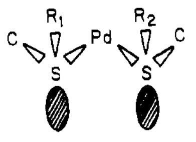
**Table II.** NMR Data on the $CH_3S$ Protons[a]

| $S_4$ | $\delta$,[b] ppm | $\Delta$,[c] ppm | $^3J_{Pt-H}$, Hz |
|---|---|---|---|
| | $[Pd(S_4)](ClO_4)_2$ | | |
| 2,2,2[d] | 2.73 | 0.63 | |
| 2,3,2 | 2.75 | 0.66 | |
| 3,2,3 | 2.53 | 0.43 | |
| 3,3,3 | 2.50 | 0.44 | |
| bme | 2.98 | 0.57 | |
| bmp | 3.14 | 0.73 | |
| bmb | 3.11 | 0.71 | |
| | $[Pt(S_4)](ClO_4)_2$ | | |
| 2,2,2 | 2.90 | 0.82 | 45.0 |
| 2,3,2 | 2.97 | 0.89 | 44.1 |
| 3,2,3 | 2.82 | 0.74 | 45.0 |
| 3,3,3 | 2.74 | 0.67 | 44.1 |
| bme | 3.28 | 0.82 | 37.8 |
| bmp | 3.36 | 0.90 | 43.2 |
| bmb | 3.38 | 0.92 | 44.1 |

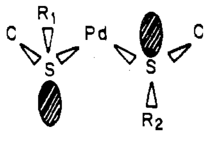
[a] Spectra run as saturated solutions in $CD_3NO_2$. [b] Chemical shift relative to internal $Me_4Si$ standard. [c] Shift on coordination relative to the free ligand signal. [d] In $Me_2SO$-$d_6$.

ferentiate with a plot of $(\Lambda_0 - \Lambda_e)$ vs. $c^{1/2}$ between a 2:1 (III) and a 4:1 (IV) electrolyte.[13] The slopes of these plots are shown in Table I and a representative plot is given in Figure 1.[10] All the slopes are in the range reported for a 2:1 electrolyte (392–465 $\Omega^{-1}$ $L^{1/2}$ $equiv^{-1/2}$)[12] except for $[Pd(bme)](ClO_4)_2$ which gave a somewhat low value. The complex $[Pd(2,2,2)](ClO_4)_2$ is insoluble in solvents suitable for a dilution study but it does dissolve in dimethyl sulfoxide. The platinum complexes appear more soluble than the palladium analogues; however, the platinum complex of 2,2,2 also has a relatively low slope value. We suggest that the low values for the bme and 2,2,2 ligands are probably due to ion association, which, in the case of $[Pd(2,2,2)](ClO_4)_2$, is very strong, requiring a very polar solvent for dissolution. Apart from $[Pd(2,2,2)](ClO_4)_2$, therefore, we have demonstrated that the complexes are monomers in which the ligand must wrap around the plane of the metal (III).

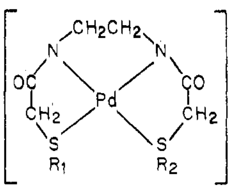
The $^1H$ NMR data are shown in Table II listing the terminal methyl protons' chemical shift relative to $Me_4Si$ ($\delta$), total shift from the free ligand resonance ($\Delta$), and for the platinum complexes the $^3J_{Pt-H}$ coupling constants. These complexes potentially have syn VI and anti VII isomers as previously demonstrated by $^1H$ NMR in the complexes VIII[14] in which interconversion between the two isomers occurs by inversion[15] at the sulfur atom, a process which occurs for monodentate and bidentate thioether ligands without dissociation of the metal–sulfur bond.[16] In this work we have proved that the syn–anti interconversion also proceeds without bond cleavage, at least in the platinum complexes, since the $^3J_{Pt-H}$ coupling is still present above the inversion temperature where only one signal for the methyl ($CH_3S$) protons is seen. This coupling has a magnitude which appears essentially invariant with temperature and also from complex to complex in this system (Table II) within experimental error, except with the ligand bme. It is interesting to note that for bidentate phosphine complexes[17-19] $J_{M-P}$ for a five-membered ring is found to be larger $J_{M-P}$ for a six-membered ring which is ascribed to a shorter metal–phosphine bond length in the relatively strain-free five-membered ring. This is consistent with the structure determinations of $[PdLCl_2]$ where L is 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane.[20] Since it is to be expected that the present tetrathioether ligands with varying backbones will be more or less strained in their attempts to wrap around the square-planar sites of the metal ions, the shift on coordination of the methyl protons was studied in an attempt to relate this to the ability of the ligand to fit around the metal.



VI



VII



VIII

$R_1 = R_2 = Et$
$R_1 = R_2 = Ph$
$R_1 = Et, R_2 = Ph$

X-ray structure determinations of complexes with bidentate thioether ligands having dimethylene backbones show that the S–M–S angle is significantly less than 90° in square-planar or octahedral complexes.[21-24] However, the six-membered ring formed by the central span of the open-chain tetradentate in the complex *u-cis*-$[Co\{H_2N(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2\}(NO_2)Cl]Cl$ gives an S–M–S angle of 92.7°.[25] A direct comparison can be drawn between the five- and six-membered ring complexes $[Pd(S\text{-methylcysteine})Cl_2]$[26] and $[Pd(\text{methionine})Cl_2]$[27] respectively having N–M–S bond angles of 87.2 and 96.88°. This suggests that for open-chain tetrathioether ligands with multimethylene backbones the best fit around a palladium(II) or platinum(II) square-planar ion would occur with either 2,3,2 or 3,2,3.[28] An analysis[3,4] of the electronic spectra of the complexes *trans*-$[Ni(S_4)I_2]$ ($S_4$ = bme, bmp, bmb, 2,2,2, 2,3,2, 3,2,3, 3,3,3) indicated that the ligand 2,3,2 had the largest in-plane contribution to the electronic spectrum suggesting that this ligand had the best total orbital overlap for the four sulfur atoms with the central metal ion. The covalent radii of octahedral nickel(II) (1.39 Å)[29] and of square-planar palladium(II) and platinum(II) (1.31 Å)[30] are comparable.

The shift of the methyl group resonance of the ligands on coordination ($\Delta$) is due to deshielding by removal of electron density from the sulfur atom, and thus the greater the shift, the more the electron density has been removed from the sulfur atom. This may be directly related to the fit of the tetrathioether ligand around the square-planar sites. It can be seen from the $\Delta$ values (Table II) that in the aliphatic ligand series, for both palladium(II) and platinum(II), the ligand 2,3,2 has the greatest shift indicating the best fit. However, 2,2,2 and not 3,2,3 has the next biggest shift. This suggests that the overriding factor determining the shift on coordination here is the relatively unstrained five-membered ring being adjacent to the methyl group. For both metal ions the $\Delta$ values for the aromatic bmp and bmb ligands are greater than for the aliphatic ligands, but this is probably mainly due to the magnetic field caused by ring currents in the aromatic parts of the ligands.[31] In accordance with this suggestion we have found that in the complexes $[MLX_2]$ (M = Pd, Pt; X = Cl, Br, I; L = $o$-$C_6H_4(SMe)_2$ and $MeSCH_2CH_2SMe$), the $\Delta$ values are larger for the aromatic ligand for a given M and X.[32] The shift values for the palladium(II) and platinum(II) bmp and bmb complexes are very similar suggesting little difference in the effect of a trimethylene compared to a tetramethylene backbone in the center of the ligand. However, the values for the ligand bme are significantly smaller suggesting a greater deviation from ideality.

The complex $[Pd(bmp)](ClO_4)_2$ was reacted in solution with excess lithium chloride which, after several hours, converted the soluble compex into the previously described[3] insoluble $[Pd_2(bmp)Cl_4]_n$ and free ligand.

In conclusion, although it has previously been found that in many cases open-chain tetradentate ligands coordinated to square-planar palladium(II) and platinum(II) prefer to bridge between metal atoms rather than form monomers with all ligand sites coordinated, we have shown that in the absence of halide ligands a large series of open-chain tetrathioether ligands with varying backbones form monomeric $[M(S_4)]^{2+}$ species. The spectroscopic properties of these species support the premise that the 2-3-2 sequence of backbone size in open-chain tetradentates coordinated around a square plane gives the minimum of strain.

**Registry No.** $[Pd(2,2,2)](ClO_4)_2$, 69501-98-0; $[Pd(2,3,2)](ClO_4)_2$, 69502-00-7; $[Pd(3,2,3)](ClO_4)_2$, 69502-02-9; $[Pd(3,3,3)](ClO_4)_2$, 69502-04-1; $[Pd(bme)](ClO_4)_2$, 69502-06-3; $[Pd(bmp)](ClO_4)_2$, 57407-95-1; $[Pd(bmb)](ClO_4)_2$, 69502-08-5; $[Pt(2,2,2)](ClO_4)_2$, 69502-10-9; $[Pt(2,3,2)](ClO_4)_2$, 69502-12-1; $[Pt(3,2,3)](ClO_4)_2$, 69502-14-3; $[Pt(3,3,3)](ClO_4)_2$, 69501-84-4; $[Pt(bme)](ClO_4)_2$, 69501-86-6; $[Pt(bmp)](ClO_4)_2$, 69501-88-8; $[Pt(bmb)](ClO_4)_2$, 69501-90-2; $Pd(CH_3CN)_2Cl_2$, 14592-56-4; $Pt(CH_3CN)_2Cl_2$, 13869-38-0.

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## Deamination of Tris(ethylenediamine)chromium(III) Thiocyanate

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The loss of ethylenediamine (en) from heated $[Cr(en)_3](NCS)_3$ offers the usual method of preparing *trans*-$[Cr(en)_2(NCS)_2]NCS$.[2] Rollinson and Bailar showed that the solid-state process is catalyzed by $NH_4SCN$.[3] The acid catalyst apparently protonates one end of a coordinated ethylenediamine molecule breaking it loose from the metal ion in the rate-determining step. Bear and Wendlandt studied this process by using thermogravimetric analysis and reported that the activation energies are 34 and 18 kcal/mol, respectively, when no catalyst is used and when $NH_4SCN$ is present.[4] These workers reported that the presence of $NH_4Br$ or $NH_4I$ had no effect on the activation energy for deamination.

Considerable study has been devoted to determining kinetic information about this reaction. From isothermal weight loss studies, activation energies of about 47.4 and 33.1 kcal/mol, respectively, were determined for the uncatalyzed and catalyzed reactions.[5] An unusual feature is that deamination of $[Cr(en)_3](NCS)_3$ produces *trans*-$[Cr(en)_2(NCS)_2](NCS)$ while deamination of $[Cr(en)_3]Cl_3$ produces a cis product.[6] However, Wendlandt and Svenum have shown that heating the tris(ethylenediamine) complexes with a large excess of $NH_4SCN$ leads to *cis*-$[Cr(en)_2(NCS)_2](NCS)$.[7] The products of these thermal matrix reactions were identified by using reflectance spectroscopy.

More recently, Akabori and Kushi[8] studied the deamination of $(+)_{589}$-$[Cr(en)_3](NCS)_3$ and $(\pm)$-$[Cr(en)_3](NCS)_3$ as catalyzed by "minute traces" of $NH_4SCN$. It was shown by elution chromatography that the product is *trans*-$[Cr(en)_2(NCS)_2]NCS$. Thus, the deamination reaction leads to a trans product when carried out in the presence of "small" amounts of catalyst but leads to a cis product when "large" amounts of catalyst are used.

As a part of our study of deamination reactions, it was noted that deamination of $[Cr(en)_3](NCS)_3$ in the presence of $NH_4SCN$ or $NH_4Cl$ lowered the activation energy but gave a different $\Delta H$ value from that when no catalyst is present.[9] We have sought to clarify this situation by using differential scanning calorimetry and thermogravimetric analysis, and this report presents results of these studies.

## Experimental Section

The thiocyanate complex was prepared from $[Cr(en)_3]_2(SO_4)_3$ which was prepared by the method of Rollinson and Bailar.[10] The $[Cr(en)_3](NCS)_3$ was obtained by dissolving 100 g of the sulfate in 275 mL of warm water and adding 147 g of solid $NH_4SCN$. After the solution was cooled, the solid product was removed by filtration. The product was recrystallized from water, washed with alcohol and ether, and air-dried. Anal. Calcd for $[Cr(en)_3](NCS)_3 \cdot H_2O$: Cr, 12.27; C, 25.50; H, 6.13; N, 29.65; S, 22.68. Found: Cr, 12.73; C, 25.43; H, 6.13; N, 29.66; S, 22.85.

Thermal studies on the deamination of $[Cr(en)_3](NCS)_3$ were carried out by using a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. Procedures used were similar to those previously described.[11] A heating rate of 10 °C/min and a nitrogen flow rate of 30 $cm^3$/min were used with samples in the range of 4–6 mg. Activation energies were determined by the method of Thomas and Clarke.[12] This procedure was used to study the initial 50–60% of the reaction, and good linear plots were obtained. Heats of reaction were obtained by comparing peak areas with those of standards using the fusion of tin.

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