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Some Transition-Metal Chelates with 8-Amino-, 8-(Diphenylphosphino)-, and 8-(Diphenylarsino)quinoline Bidentate Ligands

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Bidentate ligands containing both nitrogen and either phosphorus or arsenic donor atoms are of special importance since they utilize both σ-donating and π-accepting atoms in the same ligand. These electronic effects make such ligands suitable for the stabilization of intermediate oxidation states of transition metals. We report here the synthesis and structure of some new coordination compounds of 8-(diphenylarsino)-, 8-(diphenylphosphino)-, and 8-aminoquinolines. These mixed-donor ligand systems have been particularly chosen for their stability and for the fact that their reactions with transition-metal ions have been little investigated. No complexes of 8-(diphenylarsino)quinoline (N-As) have been hitherto reported. The reactions of 8-(diphenylphosphino)quinoline (N-P) with Ni(II) and Co(II) have been reported.[1] The reactions of 8-aminoquinoline (N-N) with several transition-metal ions have been investigated.[2] However, no complexes of (N-N) with ruthenium or rhodium have been reported. Moreover, attempts to isolate a complex of Pt(II) with (N-N) have failed.[2c] We investigated the reactions of (N-N) with Ru(II), Rh(III), Rh(I), and Pt(II) to fill this gap and to compare its behavior with that of the mixed-donor ligands.

Experimental Section

The ligands (N-As) and (N-P) were prepared by the reaction of 8-chloroquinoline with sodium metal and triphenylarsine and triphenylphosphine, respectively, in liquid ammonia.[3]

8-Aminoquinoline was prepared by the nitration of quinoline, separation of 8-nitroquinoline, and hydrogenation of this product.[4]

All complexes prepared by the procedures described below were dried under vacuum at 50 °C.

Complexes of (N-As)

(i) Dichlorobis(dimethyl sulfoxide)(8-(diphenylarsino)quinoline)ruthenium(II). To a suspension of 0.5 mmol of $Ru(Me_2SO)_4Cl_2$[5] in 10 mL of toluene was added a filtered solution of 0.5 mmol of (N-As) in 10 mL of toluene. The mixture was refluxed with continuous stirring for 2 h, during which the color changed to dark red and a light brown precipitate separated. The precipitate was filtered and washed with toluene and then with ether. The product decomposes at 265 °C. It is a nonelectrolyte in chloroform or nitrobenzene.

(ii) Trichloro(8-(diphenylarsino)quinoline)rhodium(III). To a filtered solution of $RhCl_3 \cdot 3H_2O$ (1.0 mmol) in 10 mL of H_2O was added a filtered solution of 1.0 mmol of (N-As) in 10 mL of acetone. The mixture was stirred at room temperature for 24 h. The orange-yellow precipitate that separated was filtered and washed with acetone and then with ether. It was recrystallized from chloroform as brown needles. It did not decompose or melt below 360 °C. The product is a nonelectrolyte in chloroform or DMF. The product is diamagnetic; $\chi_M = -375 \times 10^{-6}$ at 25 °C.

(iii) Di-μ-chloro-bis{chlorocarbonyl(8-(diphenylarsino)quinoline)rhodium(II)}. To a filtered solution of $[Rh(CO)_2Cl_2]$ (0.5 mmol) in 10 mL of ethanol[6,7] was added a filtered solution of 0.5 mmol of (N-As) in 10 mL of 1:1 ethanol/acetone. The solution was refluxed with continuous stirring for 2 h. The orange-yellow precipitate which separated on cooling was filtered and washed with ethanol. The product melted at 250 °C. It is a nonelectrolyte in $CHCl_3$. Molecular weight by vaporimetry in $CHCl_3$: calculated for $[Rh(N\text{-}As)(CO)Cl_2]_2$, 1118; found, 999. μ eff = 2.17 μ_B at 25 °C.

(iv) Dichloro(8-(diphenylarsino)quinoline)palladium(II). To a filtered solution of $Pd(C_6H_5CN)_2Cl_2$ (0.5 mmol) in 10 mL of acetone was added a filtered solution of 0.1 mmol of (N-As) in 20 mL of acetone. Bright yellow crystals separated on standing. The product was filtered and washed with acetone; mp 330 °C with decomposition. The product is a nonelectrolyte in $CHCl_3$.

(v) Dichloro(8-(diphenylarsino)quinoline)platinum(II). To a filtered solution of 0.5 mmol of K_2PtCl_4 in 10 mL of H_2O was added a filtered solution of 0.5 mmol of (N-As) in 20 mL of acetone. An orange-yellow precipitate separated immediately. The mixture was stirred at room temperature for 1 h. The product was filtered and washed with acetone. The product decomposes at 315 °C. It is a nonelectrolyte in DMF.

Complexes of (N-P)

(i) Reaction of (N-P) with $Ru(Me_2SO)_4Cl_2$. The reaction of (N-P) with $Ru(Me_2SO)_4Cl_2$ was investigated under conditions similar to those described for the preparation of $Ru(Me_2SO)_2(N\text{-}As)Cl_2$. However, no Ru-(N-P) complex was obtained. Instead, the dimeric complex $Ru_2(Me_2SO)_5Cl_4$ was formed. The reaction was repeated without the addition of (N-P), and again $Ru_2(Me_2SO)_5Cl_4$ was obtained. The compound is orange-yellow; mp 250 °C with decomposition. It is a nonelectrolyte in $CHCl_3$ or nitrobenzene.

(ii) Dichloro(8-(diphenylphosphino)quinoline)rhodium(II). To a filtered solution of 1 mmol of $RhCl_3 \cdot 3H_2O$ in 10 mL of H_2O was added a solution of 1 mmol of (N-P) in 10 mL of acetone. A yellow precipitate separated immediately. It then dissolved on heating. The solution was refluxed for 24 h during which a pale yellow precipitate was obtained. The solvent was evaporated completely under reduced pressure. The yellow-orange residue was extracted with acetone from which it was then precipitated with ether. The product decomposes at 280 °C. It is a nonelectrolyte in $CHCl_3$ or nitrobenzene. μ_{eff} = 2.31 μ_B at 25 °C.

(iii) Di-μ-chloro-bis{chlorocarbonyl(8-(diphenylphosphino)quinoline)rhodium(II)}. To a filtered solution of 0.5 mmol of $[Rh(CO)_2Cl_2]^-$ in 10 mL of ethanol[6,7] was added a filtered solution of 0.5 mmol of (N-P) in 10 mL of ethanol. The solution was refluxed for 2 h. Half of the solvent was then evaporated under reduced pressure. Upon addition of diethyl ether, a pale yellow precipitate separated. It was filtered and washed with ethanol and then with ether; mp 150 °C with decomposition. The product is a nonelectrolyte in $CHCl_3$. μ_{eff} = 2.29 μ_B at 25 °C.

(iv) Dichloro(8-(diphenylphosphino)quinoline)palladium(II). To a filtered solution of 0.5 mmol of $Pd(C_6H_5CN)_2Cl_2$ in 10 mL acetone was added a filtered solution of 1 mmol of (N-P) in 10 mL of acetone. The mixture was stirred at 40–50 °C for 2 h, during which a yellow-orange precipitate separated. The product was filtered and washed with acetone; mp 230 °C with decomposition. The product is a nonelectrolyte in pyridine.

(v) Dichloro(8-(diphenylphosphino)quinoline)platinum(II). This compound was prepared by a method identical with that described above for the preparation of $Pt(N\text{-}P)Cl_2$. The product is yellow; mp 230 °C with decomposition. It is a nonelectrolyte in nitrobenzene.

Complexes of (N-N)

(i) Dichlorobis(dimethyl sulfoxide)(8-aminoquinoline)ruthenium(II). To a suspension of 1 mmol of $Ru(Me_2SO)_4Cl_2$ in 10 mL of toluene was added a filtered solution of 1 mmol of (N-N) in 10 mL of toluene. The mixture was refluxed for 2 h. The yellow-green product that separated was filtered and washed with toluene and then with ether; mp 200 °C with decomposition. The product is a nonelectrolyte in DMF.

(ii) Trichloro(8-aminoquinoline)rhodium(III). To a filtered solution of 2 mmol of (N-N) in 10 mL of acetone was added a filtered solution of 1 mmol of $RhCl_3 \cdot 3H_2O$ in 10 mL of H_2O. The mixture was refluxed

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Table I. Elemental Analyses of the Ligands and Their Complexes

compound		% C	% H	% N	% Cl	% S
N-As	calcd	70.59	4.48	3.92		
	found	70.02	4.51	3.78		
N-P	calcd	80.51	5.11	4.47		
	found	80.54	5.06	4.31		
N-N	calcd	75.00	5.55	19.44		
	found	75.09	5.63	19.58		
$Ru(N\text{-}As)(Me_2SO)_2Cl_2$	calcd	43.80	4.09	2.04	10.36	9.34
	found	43.69	4.07	2.05	10.40	9.06
$Ru(N\text{-}N)(Me_2SO)_2Cl_2$	calcd	33.05	4.23	5.93	15.04	13.55
	found	32.33	4.19	5.83	15.57	12.87
$Ru_2(Me_2SO)_5Cl_4$	calcd	16.34	4.08		19.35	21.80
	found	16.28	3.83		19.54	21.58
$Rh(N\text{-}As)Cl_3$	calcd	44.48	2.82	2.47	18.80	
	found	43.96	2.97	2.50	18.75	
$Rh(N\text{-}P)Cl_2$	calcd	51.76	3.29	2.88	14.58	
	found	52.77	3.43	3.09	15.12	
$Rh(N\text{-}N)_2Cl_3$	calcd	43.42	3.22	11.26	21.41	
	found	43.20	3.32	11.21	21.00	
$[Rh(N\text{-}As)(CO)Cl_2]_2$	calcd	47.23	2.86	2.50	12.70	
	found	46.86	3.27	2.48	13.26	
$[Rh(N\text{-}P)(CO)Cl_2]_2$	calcd	51.26	3.11	2.72	13.79	
	found	50.56	3.36	2.79	13.62	
$Rh(N\text{-}N)_2Cl_3\cdot H_2O$	calcd	41.90	3.49	10.85	20.65	
	found	42.09	3.56	10.54	19.85	
$Pd(N\text{-}As)Cl_2$	calcd	47.15	2.99	2.61	13.28	
	found	47.11	2.98	2.61	13.17	
$Pd(N\text{-}P)Cl_2$	calcd	51.38	3.26	2.85	14.47	
	found	49.80	3.15	2.69	13.52	
$Pd(N\text{-}N)Cl_2$	calcd	33.60	2.49	8.71	22.09	
	found	34.46	2.69	8.61	21.86	
$Pt(N\text{-}As)Cl_2$	calcd	40.44	2.56	2.24	11.39	
	found	40.11	2.75	2.19	11.34	
$Pt(N\text{-}P)Cl_2$	calcd	43.52	2.76	2.41	12.26	
	found	43.24	3.05	2.88	11.97	
$Pt(N\text{-}N)Cl_2$	calcd	26.34	1.95	6.83	17.32	
	found	27.16	1.99	6.92	16.69	

with continuous stirring for 1 h. The bright yellow precipitate which separated was filtered and washed with acetone and then with ether. The product decomposes at 300 °C. The product has a molar conductivity, Λ(molar), of 33 Ω^{-1} cm^2 in DMF at 25 °C approximately corresponding to 1:1 electrolyte. The complex is diamagnetic; $\chi_M = -460 \times 10^{-6}$ at 25 °C.

(iii) Trichloroaquobis(8-aminoquinoline)rhodium(III). To a filtered solution of 1 mmol of $[Rh(CO)_2Cl_2]$ in 10 mL of ethanol was added a filtered solution of 2 mmol of (N-N) in 10 mL of ethanol. The solution was refluxed for 2 h. The pale yellow precipitate which separated was filtered and washed with ethanol and then with ether. The product decomposes at 300 °C. It is a nonelectrolyte in DMF. It is diamagnetic; $\chi_M = -510 \times 10^{-6}$ at 25 °C.

(iv) Dichloro(8-aminoquinoline)palladium(II). To a filtered solution of 2 mmol of (N-N) in 10 mL of acetone was added a filtered solution of 0.5 mmol of $Pd(C_6H_5CN)_2Cl_2$ in 10 mL of acetone. The mixture was refluxed with continuous stirring for 2 h. The yellow-orange precipitate obtained was filtered and washed with acetone and then with ether. The product did not melt or decompose below 360 °C. It is a nonelectrolyte in DMF.

(v) Dichloro(8-aminoquinoline)platinum(II). To a filtered solution of 2 mmol of (N-N) in 20 mL of acetone was added a filtered solution of 1 mmol of K_2PtCl_4 in 20 mL of H_2O. The solution was kept at 40–50 °C with continuous stirring for 2 h. The brown precipitate that separated was filtered and washed with acetone. It decomposes at 330 °C. The product is a nonelectrolyte in DMF.

The elemental analyses and the molecular weight determination were run by Pascher Mickroanalytisches Laboratorium, Bonn, Germany. The infrared spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer. The UV spectra were recorded by using a Perkin-Elmer 202 spectrophotometer. Solutions of about 10^{-5}–10^{-4} M concentration were used. Melting and decomposition points were taken by using a Mel-Temp apparatus. The conductivity measurements were carried out on a Fisher Scientific conductivity bridge, Model RC16B2, at 25 °C. The magnetic susceptibilities and moments were determined by the Gouy method.

Results and Discussion

The reactions of (N-As), (N-P), and (N-N) with Ru(II), Rh(III), Rh(I), Pd(II), and Pt(II) have been investigated. Almost all of these metal ions afford well-characterized complexes with the three ligands. The results of the elemental analyses for some of the nonmetals in the complexes are summarized in Table I.

With the exception of the complexes of (N-N) which are soluble only in pyridine and DMF, almost all of the other complexes are moderately soluble in chloroform, nitrobenzene, and DMF, slightly soluble in acetone, and insoluble in water and ethanol.

The molecular formulas have been assigned on the basis of the elemental analyses and some physicochemical measurements such as those of the infrared spectra, magnetic moments, and conductivity.

The infrared spectra of the complexes showed evidence for the presence of the respective ligands in them. The ν_{N-H}'s in the free (N-N) ligand occurring as sharp bands at 3448 and 3350 cm^{-1} were reduced by about 200 cm^{-1} upon coordination. Dimethyl sulfoxide was characterized by its $\nu_{S=O}$ which decreases by bonding of the metal to the oxygen atom and increases upon coordination through the sulfur atom.[8] The S=O stretching mode occurs at 1050 cm^{-1} in free Me_2SO. Some of the stretching frequencies relevant to the characterization of the complexes are listed in Table II.

The ultraviolet spectra of the complexes in chloroform and DMF were almost identical with those of the free ligands as shown in Table III. The fact that the spectra were determined in very dilute solutions (10^{-5}–10^{-4} M) imposed by the low solubility of the complexes is partly responsible for this. The d–d transitions are not intense enough to appear under these

Table II. Some Stretching Frequencies Occurring in the Infrared Spectra of the Complex

complex	str freq, cm^{-1}			
	M–Cl	S=O	C≡O	N–H
$Ru(Me_2SO)_4Cl_2$	335, 310	1105, 1080, 920		
$Ru_2(Me_2SO)_5Cl_4$	340, 260, 230	1110. 1090, 928, 910, 965		
$Ru(N\text{-}As)(Me_2SO)_2Cl_2$	340, 320	1087, 1077, 910		
$Ru(N\text{-}N)(Me_2SO)_2Cl_2$	325	1070, 917		3160
$Rh(N\text{-}As)Cl_3$	345, 320, 270, 245			
$Rh(N\text{-}P)Cl_2$	335, 308			
$[Rh(N\text{-}N)_2Cl_2]Cl$	335, 310			3180, 3100
$[Rh(N\text{-}As)(CO)Cl_2]_2$	320, 230		2040, 1970	
$[Rh(N\text{-}P)(CO)Cl_2]_2$	310, 270		2060, 1975	
$Rh(N\text{-}N)_2Cl_3\cdot H_2O$	335, 308			3350, 3120, (O–H, 3595)
$Pd(N\text{-}As)Cl_2$	334, 318			
$Pd(N\text{-}P)Cl_2$	334, 325			
$Pd(N\text{-}N)Cl_2$	330, 320			
$Pt(N\text{-}As)Cl_2$	330, 300			
$Pt(N\text{-}P)Cl_2$	310, 290			
$Pt(N\text{-}N)Cl_2$	338, 332			

Table III. Ultraviolet Spectra of the Ligands and Their Complexes (nm)

complex	in $CHCl_3$	in DMF
N-As	248, 318	270, 317
$Ru(N\text{-}As)(Me_2SO)_2Cl_2$	242, 325	
$Rh(N\text{-}As)Cl_3$		280, 318
$[Rh(N\text{-}As)(CO)Cl_2]_2$	246, 320	
$Pd(N\text{-}As)Cl_2$	245, 305, 318	
$Pt(N\text{-}As)Cl_2$		273, 310
N-P	252, 318	270, 320
$Rh(N\text{-}P)Cl_2$	244, 322	
$[Rh(N\text{-}P)(CO)Cl_2]_2$	243, 320	
$Pd(N\text{-}P)Cl_2$	246, 315	
$Pt(N\text{-}P)Cl_2$		273, 311
N-N	251, 340	268, 350
$Ru(N\text{-}N)(Me_2SO)_2Cl_2$	246, 295	
$[Rh(N\text{-}N)_2Cl_2]Cl$		282
$Rh(N\text{-}N)_2Cl_3 \cdot H_2O$		278, 318
$Pd(N\text{-}N)Cl_2$		278
$Pt(N\text{-}N)Cl_2$		285
$Ru_2(Me_2SO)_5Cl_4$	244	

conditions. All the UV bands reported are of high intensity ($\epsilon \sim 4000\text{–}9000$).

Reactions of $Ru(Me_2SO)_4Cl_2$. It has been reported[5] that $Ru(Me_2SO)_4Cl_2$ is monomeric in chloroform at 25 °C, is a nonelectrolyte in nitromethane, and has a trans configuration. When a solution of a ligand containing phosphorus or nitrogen donor atom is treated with $Ru(Me_2SO)_4Cl_2$, only two of the Me_2SO molecules are displaced.[5] Consistent with these observations, we found that (N-As) and (N-N) yield the complexes $Ru(Me_2SO)_2(N\text{-}As)Cl_2$ and $Ru(Me_2SO)_2(N\text{-}N)Cl_2$, respectively. The infrared spectra of both complexes show $\nu_{S=O}$ at 1070–1080 and 910–915 cm^{-1} corresponding to S-bonded and O-bonded Me_2SO ligands, respectively. The ν_{N-H} of the (N-N) complex appears at 3160 cm^{-1}, suggesting that the NH_2 group is bonded to ruthenium. Both complexes are nonelectrolytes in DMF at room temperature. These facts indicate that the two complexes are octahedral, with probably a trans configuration with respect to the chloride ligands (after the parent complex *trans*-$Ru(Me_2SO)_4Cl_2$).

The reaction of (P-N) with $Ru(Me_2SO)_4Cl_2$, however, did not afford a (P-N)–Ru complex. Instead, the dimeric complex $Ru_2(Me_2SO)_5Cl_4$ was obtained. The fact that no (N-P) is involved in the complex is confirmed by the absence of the bands characteristic of the ligand from the UV and IR spectra of the complex. A control experiment carried out in absence of the ligand (P-N) gave an identical diruthenium compound. The dimer is a nonelectrolyte in chloroform. Its infrared spectrum shows, in addition to absorption in the $\nu_{S=O}$ region corresponding to O-bonded and S-bonded Me_2SO, a strong band at 965 cm^{-1} which may be assigned to bridging Me_2SO. Moreover, the IR spectrum shows ν_{Ru-Cl}'s characteristic of terminal (340 cm^{-1}) and bridging (260, 230 cm^{-1}) Ru–Cl's. We propose that the dimer involves one Me_2SO and two Cl bridges.

The difference in the behavior of $Ru(Me_2SO)_4Cl_2$ with the three ligands under investigation may be attributable to the competition between dimerization and substitution reactions. Substitution in the case of (N-N) and (N-As) seems to be faster, while dimerization is faster than substitution with (N-P).

Reactions of $RhCl_3 \cdot 3H_2O$. The three ligands did not behave identically in their reactions with $RhCl_3 \cdot 3H_2O$. 8-(Diphenylarsino)quinoline afforded the complex $Rh(N\text{-}As)Cl_3$, based on its elemental analyses and on the fact that it is a nonelectrolyte in DMF. The presence of rhodium as Rh(III) is also confirmed by the fact that the complex is diamagnetic. Since pentacoordination is not common for Rh(III), it seems feasible to propose a dimeric structure for this complex, with two bridging chlorines and with an octahedral arrangement around each rhodium atom. This is supported by the fact that the IR spectrum of the complex shows absorption bands at 345 and 320 cm^{-1} due to terminal Rh–Cl and at 270 and 245 cm^{-1} due to bridging Rh–Cl. Unfortunately, this suggestion could not be tested by molecular weight determination because of the low solubility of the complex.

8-(Diphenylphosphino)quinoline afforded the tetracoordinate complex $Rh(N\text{-}P)Cl_2$ upon its reaction with $RhCl_3 \cdot 3H_2O$. The complex is most likely square planar. It is paramagnetic ($\mu_{eff} = 2.17\ \mu_B$) with one unpaired electron, consistent with the +2 oxidation state of Rh. A similar paramagnetic square-planar Rh(II) complex, namely, *trans*-$Rh\{(o\text{-tolyl})_3P\}_2Cl_2$ has been reported.[9] The IR spectrum of $Rh(N\text{-}P)Cl_2$ shows two Rh–Cl stretching bands at 335 and 308 cm^{-1} consistent with the cis arrangement of the two chloride ligands in the molecule.

8-Aminoquinoline behaved typically and gave the diamagnetic complex $Rh(N\text{-}N)_2Cl_3$. The infrared spectrum shows ν_{N-H} at 3180 cm^{-1}, indicating that (N-N) behaves as a bidentate ligand in the complex. The conductivity of a DMF solution of the complex shows that it is a 1:1 electrolyte. The complex is therefore formulated as $[Rh(N\text{-}N)_2Cl_2]Cl$. The bipyridyl complex, $[Rh(bpy)_2Cl_2]Cl$, has been prepared under similar conditions.[10] The ν_{Rh-Cl}'s in the infrared spectrum of $[Rh(N\text{-}N)_2Cl_2]Cl$ at 335 and 310 cm^{-1} suggest that it has a cis configuration.

The difference in the behavior of $RhCl_3 \cdot 3H_2O$ in its reaction with the three ligands may be attributed to their relative σ-donating and π-accepting tendencies. The relatively strong σ-donation in (N-N) results in its stabilization of the higher (+3) oxidation state of Rh. Although P and As have been reported to have comparable π-accepting tendencies, the (N-P) ligand seems to have a stronger overall π-accepting and weaker σ-donating abilities than (N-As). Thus (N-P) and not (N-As) stabilizes the +2 oxidation state. If ligands with pure P or As donor atoms were used, Rh would have been reduced all the way to the +1 oxidation state. The fact that $(o\text{-tolyl})_3P$ stabilizes the +2 state[9] may be due to the fact that the inductive effect of the methyl groups modifies the σ-donating–π-accepting tendencies of P to make them just suitable for the stabilization of the +2 oxidation state. In other words, the methyl groups played the electronic role of the N atom in the present mixed-donor ligands.

Reactions of $[Rh(CO)_2Cl_2]^-$. The anion $[Rh(CO)_2Cl_2]^-$ is an important precursor for many Rh(I) complexes. The reaction of this anion with the ligands under investigation proved to be an exception to this generalization. It seems that the mixed-donor bidentate ligands (N-As) and (N-P) tend to stabilize the +2 over the +1 oxidation state. This may be attributed to the opposing tendencies of the strong π-accepting P and As atoms to stabilize the low oxidation state (+1) and the strong σ-donating, weak π-accepting N to stabilize the higher oxidation state (+3). The presence of CO in the Rh complexes nullifies the electronic difference which was observed between (N-As) and (N-P) in their reactions with $RhCl_3$.

The ligands (N-As) and (N-P) afford the dimeric complexes $[Rh(N\text{-}As)(CO)Cl_2]_2$ and $[Rh(N\text{-}P)(CO)Cl_2]_2$, respectively. Both complexes are nonelectrolytes in DMF. They show strong bands in their infrared spectra at 2040, 1970 and 2060, 1975 cm^{-1}, respectively, indicative of terminal carbonyls. Both complexes are low-spin paramagnetic ($\mu_{eff} = 2.29\ \mu_B$ for the (N-As) complex and $\mu_{eff} = 2.31\ \mu_B$ for the (N-P) complex), suggesting no Rh–Rh bonding in the dimers. Thus, bridging most likely occurs via the Cl atoms as supported by the evidence from the IR spectra of the complexes which show absorption due to terminal and bridging Rh–Cl. Moreover, molecular weight determination for the (N-As) complex shows 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 ν_{N-H} bands at 3350 and 3120 cm^{-1}, indicative of free and coordinated NH_2, respectively (in addition to ν_{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 ν_{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 ν_{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 ν_{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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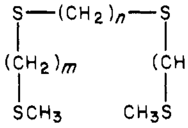
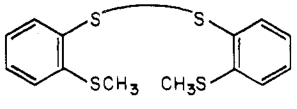
We have been interested for some time in the coordination chemistry of thioether ligands and have previously reported that the open-chain tetrathioethers I and II are unable to replace all the halide ligands around palladium(II) and platinum(II) to form monomeric complexes $[M(S_4)]X_2$ in which S_4 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

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