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Solid-State Isomerism and Intermetallic Interactions in Rhodium(I) Carbonyl–Amine Complexes

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The halogen-bridged rhodium(I) carbonyl halides, $[Rh_2X_2(CO)_4]$ (X = Cl or Br), undergo a typical bridge-splitting reaction when treated with ammonia or amines, yielding compounds of the type $[RhX(CO)_2(Amine)]$ which are remarkable for the striking variety of their colors. In the present study, the color–structure relationship of these complexes was investigated by a variety of spectroscopic techniques, utilizing a series of some fifty species specifically prepared to include a variety of primary, secondary and heteroaromatic amines. It was found that in solution all complexes exist as non-ionic, monomeric, square-planar entities, whereas in the crystalline state two forms are possible. In one form the individual coordination entities closely resemble those present in solution and thus are essentially independent of each other. In the other form, the coordination entities interact through the Rh(I) centers and their optical spectra indicate electron delocalization leading to unidimensional complex chains. The electronic spectral pattern of these complexes may be considered to be a diagnostic feature for square planar d^8 systems with axial metal–metal interactions.

Introduction

The bridge-splitting reaction of rhodium(I) carbonyl halides, $[Rh_2X_2(CO)_4]$ (X = Cl or Br), with ammonia and a variety of amines was first reported by Vallarino [1] in 1959. In that early report it was observed that the reaction yields crystalline products which all have the same general coordination formula, $[RhX(CO)_2(Amine)]$, but exhibit a wide variety of colors ranging from intense purple to pale yellow. It was suggested that the dark-colored complexes might involve some kind of metal–metal interaction, similar to that believed to exist [2–6] in Magnus' green salt $[Pt(NH_3)_4][PtCl_4]$; however, no concrete evidence could be offered in support of this suggestion. Subsequently, a number of $[RhX(CO)_2(Amine)]$ complexes were reinvestigated by Wilkinson [7] and by Pannetier [8–11], who again remarked on the striking diversity of their colors. Similar observations were later reported by Ugo, Bonati and coworkers [12–13] in their thorough study of the equilibrium reaction between $[Rh_2Cl_2(CO)_4]$ and nitriles; these authors were actually able to isolate two interconvertable isomeric forms – one yellow and the other purple – for the benzylcyanide and phenylcyanide complexes of general formula $[RhX(CO)_2(NCR)]$. All of these investigators, although concurring in the suggestion that the dark-colored form of these complexes must involve some kind of metal–metal interaction, could not provide any identifying evidence for it and could not offer any explanation for the existence of the different crystalline forms.

Three factors have led us to look with renewed interest at this problem and to undertake the present investigation. First, there has been a growing concern over 'unidimensional complexes' [14] and their potential as anisotropic electronic conductors. Second, the in-depth studies carried out by D. S. Martin's group [15–19] on the metal–metal interactions of some Pt(II) complexes have provided the previously missing experimental and theoretical bases for the understanding of this type of systems. Third, our recent work on the square planar complexes of Ni(II) with 2,6-substituted (doubly hindered) pyridine ligands have led us to recognize that these ligands, once coordinated to a metal ion in a square planar environment, effectively block any access to its axial positions [20]. In the case of the $[RhX(CO)_2(Amine)]$ complexes, therefore, coordination of these doubly hindered pyridine ligands may be expected to prevent the formation of metal–metal bonding and thus provide a reference point for the structural study of related species. Based on these considerations, we set out to investigate a wide selection of $[RhX(CO)_2(Amine)]$ complexes, in which the halogen as well as the amine were systematically varied in an attempt to elucidate the structural reasons leading to the different colors of the crystalline species.

Experimental

Starting Materials

$[Rh_2Cl_2(CO)_4]$ and $[Rh_2Br_2(CO)_4]$ were prepared according to Hieber [21] and recrystallized from boiling hexane. Amines were analytical reagent grade products which were dried over Linde 4A molecular sieves and further purified by distillation or crystallization, immediately before use.

General Procedures

Conductivity measurements were carried out with a Serfass Model RCM 15 Conductivity Bridge, in acetone solution at 25 °C. *Magnetic susceptibility measurements* were made by the Gouy method on powdered solids at room temperature. *Melting points or decomposition temperatures* were determined under a microscope equipped with reflected light. *Infrared spectra* were recorded with Perkin Elmer Models 521, 621 and 580 Spectrophotometers. The samples were examined as mulls in Nujol and hexachlorobutadiene, and also in dichloromethane solution. *Ultraviolet and visible absorption spectra* were recorded with Cary Models 14 and 17 Spectrophotometers, both in dichloromethane solution and in the solid state. The solid samples were examined by diffuse reflectance as well as by transmission, using Nujol mulls and transparent films (obtained by evaporation of a dichloromethane solution on a quartz disk). *Proton NMR spectra* were recorded at room temperature with a Varian EM 390 Spectrometer, using deuterochloroform as the solvent. *Carbon-13 NMR spectra* were obtained with a Varian CFT20 Spectrometer. *Mass spectra* of several complexes were obtained with a DuPont 21-491B Mass Spectrometer.

Preparation of the [RhX(CO)₂(Amine)] Complexes

Chlorodicarbonylamminerhodium(I)

A solution of dry gaseous ammonia in hexane was added dropwise and with stirring to a solution of $[Rh_2Cl_2(CO)_4]$ (0.5 g) in hexane (100 ml) at room temperature. The addition of the ammonia solution caused the immediate separation of a purple gelatinous precipitate. The addition was continued until a drop of the mother liquor no longer formed the typical orange needles of $[Rh_2Cl_2(CO)_4]$ when evaporated under a microscope. The purple precipitate was filtered with suction, washed with hexane, and recrystallized from boiling chloroform. The compound (0.45 g) was obtained as fiber-like green needles with a metallic sheen, which on grinding gave a purple powder. The infrared spectra (4000–200 cm^{-1}) of this complex and of its bromo-analog are shown in Table IV, together with their complete assignments.

Other [RhX(CO)₂(Amine)] Complexes

All chloro-compounds were prepared by the general procedure described for the ammonia-complex, with the following modifications: (a) In the preparation of compounds containing primary alkylamines, care was taken to avoid an excess of the amine, which would cause decomposition of the desired complex. With arylamines, an excess of ligand did not affect the reaction. (b) Since the amine-complexes were generally more soluble than the ammonia-complex, it was often necessary to concentrate the original solutions to a small volume under reduced pressure and/or cool them to 0 °C, in order to complete the precipitation of the products. Also, the amine-complexes were best recrystallized from hexane or from dichloromethane by dilution with hexane. (c) A change in the reaction medium (hexane, benzene, diethylether, dichloromethane, or chloroform) had no effect on either the formula or the color of the crystalline products with one exception: for 2-naphthylamine, two isomeric crystalline forms were obtained – one dark yellow (from hexane) and the other purple (from dichloromethane or chloroform). The two isomers gave identical solutions in dichloromethane or chloroform; addition of hexane to these solutions caused immediate precipitation of the yellow form which then rapidly changed to the purple one.

The bromo-compounds were prepared in two ways: (a) By action of the amine on a solution of the bromocarbonyl, $[Rh_2Br_2(CO)_4]$, as described for the chloro-compound; and (b) From the chloro-compounds by exchange with lithium bromide in acetone, as in the following example: A solution of the yellow $[RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)]$ in acetone was treated with an excess of lithium bromide. No change in the color of the solution was observed, but after roto-evaporation to dryness, a violet residue was obtained. This was dissolved in dichloromethane and the yellow solution was filtered and diluted with hexane. Violet-green needles formed (yield, 80%), which were identified as $[RhBr(CO)_2(p\text{-}CH_3C_6H_4\text{-}NH_2)]$ by comparison with a sample prepared from $[Rh_2Br_2(CO)_4]$ and *p*-toluidine. In the preparation of the bromo-complexes, yields ranged from 95% to 50%, the lower values corresponding to the more soluble compounds. Attempts to prepare iodo-derivatives from the chloro-compounds by exchange with lithium iodide in acetone resulted in brown oily residues, from which no definite complexes could be isolated.

Properties of the [RhX(CO)₂(Amine)] Complexes

Physical Properties

Colors, crystal forms, decomposition temperatures, and analytical data of the complexes are listed

TABLE I. Colors, Crystal Forms, Decomposition Temperatures and Analytical Data for Some [RhX(CO)$_2$(Amine)] Complexes.

Amine	Color[a]	X	Decomp. temp. (°C)	Analytical Data								Molecular Weight	
				Nitrogen, %		Halogen, %		Carbon monoxide, %		Rhodium, %		Found	Calcd
				Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.		
Ammonia	purple, golden green	X = Cl[b]	145	6.4	6.6	16.75	16.8	26.9	26.5	49.1	48.7		
	purple-red, golden	X = Br[b]	128	5.8	5.5	31.3	31.2	21.7	21.9	40.25	40.2		
Methylamine	violet, green	X = Cl[b]	144	6.3	6.1	15.6	15.5	24.4	24.85			240.0[f]	228.4
	violet, gray-green	X = Br[b]	131	5.45	5.2	29.8	29.6	20.3	20.75			279.0[f]	269.9
Ethylamine	violet, green	X = Cl[b]	149	5.6	5.85	14.9	14.8	23.8	23.4				
	violet, golden green	X = Br[b]	130	4.9	4.9	28.35	28.1	19.6	19.7				
n-Propylamine	blue, green	X = Cl[b]	102	5.65	5.5	14.1	14.0	20.0	22.1			270.1[f]	253.5
	purple, golden green	X = Br[b]	91	4.75	4.7	26.6	26.8	18.5	18.8			310.5[f]	298.0
iso-Propylamine	brown-violet, golden	X = Cl[c]	97	5.8	5.5	13.7	14.0	22.4	22.1				
	brown-violet, golden	X = Br[c]	88	4.85	4.7	26.9	26.8	19.0	18.8				
n-Butylamine	violet, green	X = Cl[b]	111	5.0	5.2	13.0	13.25	21.3	20.9				
	violet, green	X = Br[b]	105	4.6	4.5	25.6	25.6	17.5	17.95				
Cyclohexylamine	blue, gray green	X = Cl[b]	78	4.95	4.8	12.35	12.1	19.5	19.1				
	blue, green	X = Br[b]	75	4.1	4.15	23.2	23.6	16.4	16.6				
Benzylamine	blue, bronze	X = Cl[b]	131	4.6	4.65	12.0	11.8	18.2	18.6				
	violet, green	X = Br[b]	121	4.3	4.05	23.0	23.1	16.2	16.2				
Aniline	violet, golden green	X = Cl[b]	168	4.75	4.9	12.6	12.3	19.0	19.5	35.6	35.8	279.0[f]	287.5
	purple-red, golden	X = Br[b]	127	4.15	4.2	24.4	24.1	16.7	16.9	31.3	31.0	348.6[f]	332.0
o-Toluidine	bright yellow	X = Cl[b]	113	4.5	4.6	11.7	11.75	18.5	18.6	34.3	34.1	298.0[f]	301.5
	bright yellow	X = Br[d]	98	4.3	4.0	22.8	23.1	16.5	16.2	29.5	29.7	351.0[f]	346.0
m-Toluidine	bright red	X = Cl[b]	140	4.8	4.6	11.9	11.75	19.0	18.6	34.3	34.1	316.9[f]	301.5
	bright red	X = Br[b]	120	4.2	4.0	22.9	23.1	16.6	16.2	30.1	29.7	330.0[f]	346.0
p-Toluidine	bright yellow	X = Cl[b]	139	4.7	4.6	11.6	11.75	18.5	18.6	34.0	34.1	280.0[f]	301.5
	purple, golden green	X = Br[b]	130	4.0	4.0	22.9	23.1	16.0	16.2	29.5	29.7	360.6[f]	346.0
o-Anisidine	pale yellow	X = Cl[b]	112	4.3	4.4	11.0	11.2	17.5	17.6				
	pale yellow	X = Br[b]	101	4.0	3.9	22.5	22.1	15.1	15.5				
m-Anisidine	purple, golden green	X = Cl[b]	129	4.45	4.4	11.6	11.2	17.9	17.6				
	purple, golden green	X = Br[b]	117	4.1	3.9	22.0	22.1	15.7	15.5				
p-Anisidine	violet, bronze	X = Cl[e]	147	4.6	4.4	11.5	11.2	17.1	17.6				
	red, golden green	X = Br[e]	107	3.9	3.9	22.6	22.1	15.0	15.5				
1-Naphthylamine	yellow	X = Cl[d]	159	4.0	4.15	10.25	10.5			30.9	30.5	350.0[g]	337.6
	yellow	X = Br[d]	145	3.6	3.7			14.9	14.7	27.2	26.9		
2-Naphthylamine	purple or yellow[h]	X = Cl[b]	150	4.1	4.15	10.3	10.5	16.5	16.6	30.6	30.5	351.3[g]	337.6
	brown, metallic shine	X = Br[d]	143	3.85	3.7			14.5	14.7	26.4	26.9		
di-iso-Propylamine	pale yellow	X = Cl[e]	103	4.5	4.7	12.3	12.0	19.1	18.95				
	pale yellow	X = Br[e]	83	3.9	4.1	23.1	23.5	16.3	16.5				

(continued overleaf)

TABLE I. *(continued)*

Amine	Color[a]	X	Decomp. temp. (°C)	Analytical Data								Molecular Weight	
				Nitrogen, %		Halogen, %		Carbon monoxide, %		Rhodium, %		Found	Calcd.
				Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.		
Dibenzylamine	pale yellow	X = Cl[d]	113	3.4	3.6			14.3	14.3	26.6	26.3	370.0[g]	391.7
	pale yellow	X = Br[d]	105	3.1	3.2			13.1	12.8	24.0	23.6	420.5[g]	436.1
Phenylmethylamine	violet, green	X = Cl[b]	142	4.4	4.6			19.0	18.6	34.0	34.1		
	violet, golden	X = Br[b]	140	4.2	4.05			16.4	16.1	29.6	29.7		
				Carbon, %		Hydrogen, %		Nitrogen, %					
				Found	Calcd.	Found	Calcd.	Found	Calcd.				
2,3,6-Trimethylpyridine	pale yellow	X = Cl[e]	84	38.24	38.18	3.24	3.20	4.42	4.45				
2,4,6-Trimethylpyridine	pale yellow	X = Cl[e]	86	38.22	38.18	3.24	3.20	4.42	4.45				

[a] The dark-colored solids were strongly dichroic; for these compounds, the first color listed is that observed by transmission through a thin non-oriented film, while the second color indicates the bulk appearance of the sample. [b] Fiber-like needles. [c] Elongated plates. [d] Tiny prisms. [e] Leaflets. [f] Cryoscopic in benzene. [g] Crioscopic in nitrobenzene. [h] Two isomeric forms were isolated.

in Table I. Electronic spectra are listed in Table II and infrared spectra in Tables III and IV.

The $[RhX(CO)_2(Amine)]$ complexes had no detectable vapor pressure nor did they show any tendency to reform the (volatile) parent carbonyl-halide when heated. Their mass spectra gave a random decomposition pattern, with no evidence of oligomers or of the monomeric parent ion. All $[RhX(CO)_2(Amine)]$ complexes were moderately to very soluble in dichloromethane, chloroform, nitrobenzene, methanol and ethanol; sparingly soluble in benzene, ethyl ether, and hexane; insoluble in water. The solutions were very pale yellow when freshly prepared; on standing, they darkened after a few hours and eventually decomposed forming dark-colored, amorphous precipitates. The most soluble complexes (*e.g.* those of iso-propyl-, di-iso-propyl-, and cyclohexyl-amine) usually gave the least stable solutions.

The ^1H NMR spectra of the complexes in deuterochloroform showed the protons of the coordinated amines as relatively sharp peaks shifted by as much as 2 τ upfield relative to the free amine (*e.g.*:*p*-toluidine, 4.8 τ; $[RhCl(CO)_2(p\text{-toluidine})]$, 6.7 τ). The ^{13}C NMR spectra showed no detectable peaks for the two carbonyl environments, using samples of natural ^{13}C abundance; the signals of the coordinated amines were observed but gave little relevant information.

Yellow and Purple Isomers of [RhCl(CO)₂(2-naphtylamine)]

The infrared spectra of the two isomers showed only minor differences between 2500 and 250 cm^{-1}, but exhibited marked variations in the -NH_2 stretching region ($\nu(NH_2)$: 2-naphthylamine, 3400, 3320, 3210; $[RhCl(CO)_2(2\text{-naphthylamine})]$, yellow isomer: 3270, 3185, 3110; purple isomer: 3250 cm^{-1}). In solution, the two isomers gave identical spectra ($\nu(NH_2)$: 3260, 3220 cm^{-1}; ^1H NMR: NH_2 for 2-naphthylamine, 4.9 τ; for $[RhCl(CO)_2(2\text{-naphthylamine})]$, 6.4 τ).

Chemical Behavior

The $[RhX(CO)_2(Amine)]$ complexes were found to be chemically very reactive. In addition to the chlorine-by-bromine exchange previously described, the complexes underwent a wide range of substitution reactions often followed by loss of carbon monoxide. For example, when a methanol solution of the amine complex was treated with concentrated hydrochloric acid, the $[RNH_3]^+[RhCl_2(CO)_2]^-$ [22] species were formed. In turn, reaction with triphenylphosphine gave $[RhCl(CO)(Ph_3P)_2]$ [23] and reaction with p-methoxyphenylisocyanide (CNR) in the presence of perchlorate ions, yielded $[Rh(CNR)_4]\cdot ClO_4\cdot C_2H_5OH$ [24]. Thus, the general reactivity of the $[RhX(CO)_2(Amine)]$ species in solution is extremely similar to that of the parent

TABLE II. Representative Electronic Spectra of the [RhX(CO)$_2$(Amine)] Complexes in the Solid State and in Dichloromethane Solution.[a]

Amine, X	Soln.[b]	Solid[c]	Amine, X	Soln.[b]	Solid[c]
Solids with Rh–Rh interactions among 'stacked' units					
Ammonia, Cl	263	257	*o*-Toluidine, Cl	256	–
	337	–		330	–
	–	560–615[d]		–	440
Ammonia, Br	262		*m*-Toluidine, Cl	263	–
	320	–		332	–
	–	540–550[d]		–	530
Methylamine, Cl	267	257	*p*-Toluidine, Cl	255	280 sh
	337	–		338	–
	–	600		–	450
Ethylamine, Cl	261	256	*p*-Toluidine, Br	240	270
	337	–		330	–
	–	615		–	550
n-Propylamine, Cl	263	267 sh	*p*-Anisidine, Cl	252	280 sh
	336	–		335	–
	–	590		–	615
n-Hexylamine, Cl	250	250	2-Naphthylamine, Cl	260	262
	330	–	(yellow)	332	–
	–	605		–	440
Benzylamine, Cl	252	260	2-Naphthylamine, Cl	260	262
	335	–	(purple)	332	–
	–	650		–	620
Solids with non-interacting units					
2-Methylpyridine, Cl	275	252	2,6-Dimethylpyridine, Cl	264	270
	335	340		337	330
di-Iso-propylamine, Cl	251	252	2,6-Dimethylpyridine, Br	265	262
	339	325		335	336
2,3,6-Trimethylpyridine, Cl	271	–	2,4,6-Trimethylpyridine, Cl	262	255
	337	337		341	340

[a] Absorption maxima are given as wavelength (nm). [b] Compounds were examined in dichloromethane solution at room temperature. [c] The reported values are those obtained by transmission from Nujol mulls of the complexes. Thin films of the complexes evaporated on quartz plates from dichloromethane solutions gave identical spectra. [d] The position of the absorption maximum varied slightly depending upon mull preparation.

TABLE III. Carbonyl Stretching Frequencies (cm^{-1}) of the [RhX(CO)$_2$(Amine)] Complexes.

Amine	X	ν(CO) symm.		ν(CO) antisym.	
Solids with Rh–Rh interactions among 'stacked' units[a]					
n-Propylamine	Cl	2090 vs	2053 w	2030 vs	1976 m
	Br	2075 vs	2053 w		
n-Butylamine	Cl	2075 vs	2049 w	2000 vs	
Cyclohexylamine	Cl	2087vs	2066 w	2000 vs	
	Br	2079 vs	2053 w	1980 vs	
Benzylamine	Cl	2090 vs	2062 w	2010 vs	1996 m
	Br	2079 vs	2058 m	2020 vs	1990 m
Aniline	Cl	2092 vs	2078 m	2020 vs	2010 sh
	Br	2083 vs	2058 w	2008 vs	
o-Toluidine	Cl	2100 vs	2088 sh	2028 vs	
	Br	2105 vs		2028 vs	

(continued overleaf)

TABLE III. *(continued)*

Amine	X	ν(CO) symm.		ν(CO) antisym.	
m-Toluidine	Cl	2092 vs	2061 vw	2032 vs	1990 vw
	Br	2083 vs	2062 vs	2020 vs	1990 w
p-Toluidine	Cl	2094 vs		2036 vs	1998 sh
	Br	2094 vs	2066 w	2033 vs	1994 m
m-Anisidine	Cl	2096 vs	2066 sh	2037 vs	1996 sh
p-Anisidine	Cl	2092 vs	2062 sh	2032 vs	1988 w
	Br	2096 vs	2070 sh	2032 vs	2000 w
Pyrazine	Cl	2105 vs	2075 sh	2010 vs	1960 w
	Br	2080 vs		2002 vs	
1-Naphthylamine	Cl	2088 vs	2065 sh	2008 vs	1995 w
2-Naphthylamine	Cl yellow	2093 vs	2062 w	2037 vs	2007 w
	Cl purple	2097 vs	2068 w	2025 vs	1985 w
	Br	2092 vs	2064 w	2026 vs	1986 w
Solids with 'non-stacked' units[a]					
di-Isopropylamine	Cl	2075 vs		2000 vs	
	Br	2070 vs		1996 vs	
o-Anisidine	Cl	2079 vs		1990 vs	
	Br	2075 vs		1988 vs	
2,6-Dimethylpyridine	Cl	2080 vs		2002 vs	
2,3,6-Trimethylpyridine	Cl	2080 vs		2005 vs	
2,4,6-Trimethylpyridine	Cl	2180 vs		2100 vs	
Solutions[b]					
Ammonia	Cl	2093 vs		2014 vs	
	Br	2090 vs		2012 vs	
Aniline	Cl	2094 vs		2018 vs	
o-Toluidine	Cl	2094 vs		2018 vs	
m-Toluidine	Cl	2094 vs		2016 vs	
p-Toluidine	Cl	2094 vs		2016 vs	
	Br	2092 vs		2018 vs	
p-Anisidine	Cl	2094 vs		2016 vs	
1-Naphthylamine	Cl	2100 vs		2023 vs	1990 sh

[a] In Nujol mull or thin solid film: s = strong, m = medium, w = weak, br = broad, v = very. [b] In dichloromethane.

TABLE IV. Infrared Absorption Frequencies (cm^{-1}) of the [RhX(CO)$_2$(NH$_3$)] Complexes Between 4000 and 250 cm^{-1}.[a]

X = Cl	X = Br	Assignment
3328 m	3325 sh	N–H stretching
3315 m	3310 m	
3250 w	3240 w	
3205 vw	3200 vw	
3170 vw	3160 vw	
2100 vs, (2098) vs	2100 vs, (2090) vs	C–O stretching
2070 m	2070 w	
2020 vs, b (2018) vs	2030 vs, (2020) vs	
1990 w	1994 w	
1968 vw	1972 sh	
1600 m	1600 m	NH_3 degenerate deformation
1258 s	1256 m	NH_3 symmetryc deformation[b]
1242 m	1242 m	

(continued on facing page)

TABLE IV. *(continued)*

X = Cl	X = Br	Assignment
700 m	696 m	NH_3 rocking
608 s	604 s	Rh–C–O out of plane deformation
497 s	492 s	Rh–C antisymmetric stretching
462 m	467 vw	
300 s		Rh–X stretching
294 sh	294 m	

[a] s = strong, m = medium, w = weak, b = broad, v = very. Spectra taken in KBr disks and in Nujol mulls agree within experimental error. Values in parentheses refer to spectra taken in dichloromethane solution. [b] The relative intensities of these two bands vary from sample to sample.

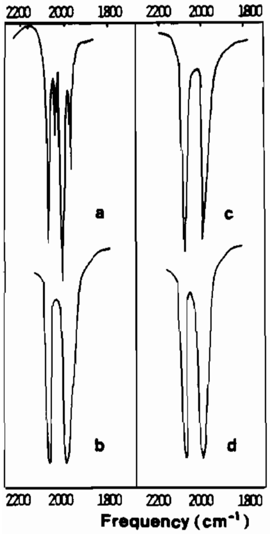

Fig. 1. Infrared spectra (CO stretching vibrations) of: (a) [$RhCl(CO)_2$(*m*-toluidine)], red solid; [$RhCl(CO)_2$(*m*-toluidine)], CH_2Cl_2 solution; (c) [$RhCl(CO)_2$(2,6-dimethylpyridine)], pale yellow solid; (d) [$RhCl(CO)_2$(2,6-dimethylpyridine)], CH_2Cl_2 solution.

carbonylhalide, and indeed for most preparative purposes the [$RhX(CO)_2$(Amine)] complexes may be used as an easy-to-handle, stabilized form of [$Rh_2X_2(CO)_4$].

Results

All the [$RhX(CO)_2$(Amine)] complexes investigated in this work were obtained as well-crystallized, non-volatile, diamagnetic solids of moderate to good thermal stability. Table I lists some identifying properties of the solid complexes and illustrates the variety of their colors; regardless of the original color of the solid, however, all complexes gave pale yellow solutions when dissolved in organic solvents. Cryoscopic and conductivity measurements showed the species present in these solutions to be non-ionic, monomeric, and undissociated. The infrared spectra of the complexes in dichloromethane solution had two strong, sharp absorptions of almost equal intensities in the carbonyl stretching region (Table III and Fig. 1b and d), indicating that the two CO ligands must be coordinated in *cis* positions to each other.

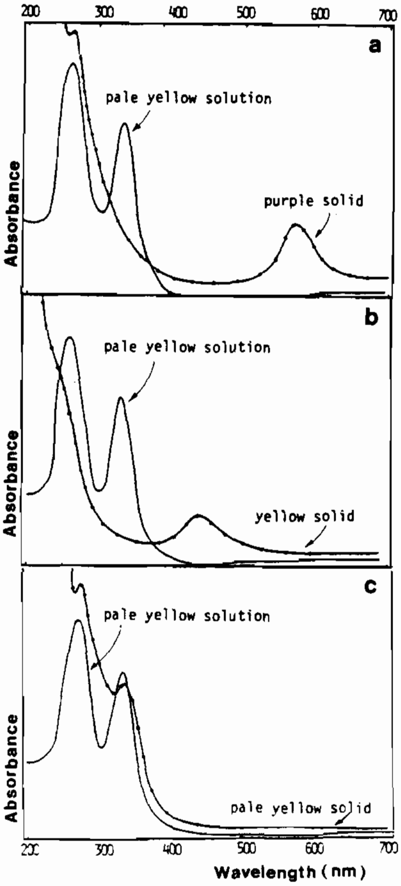

Fig. 2. Electronic absorption spectra (solid films and CH_2Cl_2 solution) of: (a) [$RhCl(CO)_2(NH_3)$]; (b) [$RhCl(CO)_2$(*p*-toluidine)]; (c) [$RhCl(CO)_2$(2,6-dimethylpyridine)].

The ^1H NMR spectra in deuterochloroform gave a single signal for the $-NH_2$ group, shifted upfield by approximately 2 τ units with respect to the free amine. These results, consistent with those reported by Pannetier for the analogous [RhX(Cod)L] complexes (Cod = 1,5-cyclooctadiene; L = 2-aminopyridine, 2-methyl-6-aminopyridine, and 2,6-diaminopyridine), confirmed the presence of a single diamagnetic species in solution and ruled out the existence of either solvation or bridge-splitting equilibria. In agreement with this conclusion, the electronic spectra of the solutions in the visible–ultraviolet region showed a rather simple pattern (Table II and Figs. 2a, b, and c), quite similar to that usually observed for four-coordinate, square planar d^8 systems.

Our investigation of the solid complexes focused on the two most significant aspects of their spectral properties – the electronic (visible–ultraviolet) spectra and the vibrational (infrared) spectra in the carbonyl stretching region. It was found that the electronic spectra of the solid complexes, observed both by diffuse reflectance and by transmission, fell into two categories. A small number of solid complexes, all pale yellow in color, showed a spectral pattern (Fig. 2c) virtually identical to that of the species in solution. The majority of the solids, however, had completely different spectra. No absorption occurred in the near ultra-violet between 350 and 320 nm, whereas a new, strong, symmetrical absorption appeared in the visible region (Figs. 2a and b), ranging in wavelength from 650 nm (purple complexes) to 425 nm (yellow complexes). The spectral pattern of these solids thus closely resembled that reported by Martin for the crystalline [$PtCl_2$-(ethylenediamine)] species, in which the square planar coordination entities were shown by single crystal X-ray diffraction to involve metal-metal interactions along the axial positions.

The infrared spectra of the solid complexes in the carbonyl stretching region also fell into two groups: The pale yellow solids whose electronic spectra resembled those of the solution showed two single, strong $\nu(CO)$ absorptions without splittings or shoulders (Fig. 1c). In contrast, the $\nu(CO)$ absorptions of all other solids exhibited a very marked splitting, often resulting in four distinct peaks (Fig. 1a), and thus indicated a reduced symmetry for the $Rh(CO)_2$ moieties of these complexes.

A significant trend was also observed for the $-NH_2$ stretching modes of the crystalline complexes, as illustrated by the yellow and purple isomeric forms of [$RhCl(CO)_2$(2-naphthylamine)]. In the spectrum of the yellow isomer, the $\nu(NH_2)$ vibrations appeared as a rather broad, split band, identical in pattern to that of the free parent amine although shifted to lower energies by some 150 cm^{-1} (Fig. 3c). In contrast, the $\nu(NH_2)$ for the purple isomer appeared as a rather strong, sharp single band (Fig. 3a). This difference in the $\nu(NH_2)$ absorption must obviously be related to the crystal lattice environment of the $-NH_2$ groups, for in dichloromethane solution both isomers gave identical spectra (Fig. 3b). Very much the same situation was observed for the other complexes of primary amines. In general, the dark colored forms exhibited single sharp $\nu(NH_2)$ absorptions, whereas the yellow forms gave broad split absorptions similar in pattern to those of the parent amines.

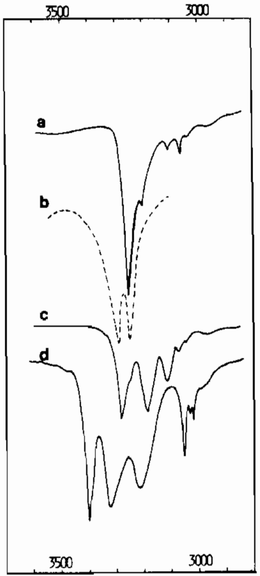

Fig. 3. Infrared spectrum ($-NH_2$ stretching absorptions) of [$RhCl(CO)_2$(2-naphthylamine)] as: (a) purple crystalline form; (b) dichloromethane solution, (c) yellow crystalline form. The NH_2 absorption of pure 2-naphthylamine is shown in (d) for comparison.

Discussion

All experimental evidence shows that the [$RhX(CO)_2$(Amine)] complexes exist in solution as independent square planar entities; as for the solids, their structures are most effectively discussed by comparison to the solutions: The few pale yellow solids whose electronic and vibrational spectra exactly match those of the solutions may be assigned a 'normal' structure, in which the square planar coordination entities are essentially independent of one another. The other group of solids, with colors ranging from deep purple to deep yellow, may instead be assigned a 'stacked' arrangement in which the planar [$RhX(CO)_2$(Amine)] entities are associated through extensive Rh–Rh interactions – a situation similar to that existing in [$PtCl_2$(ethylenediamine)] [19]. In his review of the electronic spectra of Pt(II) complexes [15], Martin has pointed out that a systematic investigation of the metal–metal electronic interactions among 'stacked' coordination entities in crystalline compounds is rendered difficult by two factors: One is the scarcity of compounds that present this phenomenon and the other is the experimental difficulty in preparing crystals suitable for crystallographic and polarized spectral studies. The series of rhodium(I) compounds reported in this paper, if obtained as crystals of suitable quality and size, might offer a unique opportunity for the study of the electronic effects resulting from even minor variations in stacking parameters. So far, however, we have encountered considerable difficulties in preparing the desired crystals, owing to the marked tendency of the [$RhX(CO)_2$(Amine)] species to crystallize as exceedingly fine, fiber-like needles.

The next question concerns the reason underlying the choice of structure – 'normal' or 'stacked' – for each [$RhX(CO)_2$(Amine)] complex. Careful examination of the many compounds investigated in this work shows no relationship between the structural type and the basicity – or more generally the electronic characteristics – of the amine ligand. Nor does the halogen present seem to have an appreciable influence, for even the few chloro- and bromo-complexes which exhibit very different colors (*e.g.* the yellow [$RhCl(CO)_2(p\text{-}CH_3C_6H_4NH_2)$] and the purple [$RhBr(CO)_2(p\text{-}CH_3C_6H_4NH_2)$]) actually belong to the same structural ('stacked') type. Rather, the determining factor in the choice of structure appears to be steric hindrance, for only those complexes in which the amine ligand has a highly hindered N-donor atom (*e.g.* 2-methylpyridine, 2,6-dimethylpyridine, *o*-anisidine) are obtained in the non-stacked form. Scale molecular models support the conclusion that these bulky ligands prevent neighboring square planar entities from approaching close enough to give appreciable intermetallic bonding. For the 'stacked' forms, hydrogen bonding interactions among adjacent entities undoubtedly further contribute to the overall stabilization of the crystal lattice.

One more question remains to be considered, namely the variety of color – from deep purple to red to bright yellow – observed for the 'stacked' forms. (This color variety reflects the dramatic shifts of the 'visible band' in the spectra of the crystalline complexes; in contrast the 'ultraviolet band' remains essentially constant.) The fact that [$RhCl(CO)_2$(2-naphthylamine)] exists as a yellow isomer (absorption at 430 nm) and a purple isomer (absorption at 620 nm) clearly indicates that the energy of the 'visible band' is not directly related to the electronic properties of either the amine or the halogen, but rather appears to depend on the type of stacking present in the crystal. Specificially, in the purple form of [$RhCl(CO)_2$(2-naphthylamine)] the NH_2 groups appear to be rigidly hydrogen bonded while in the yellow form they are obviously less constrained and approach the symmetry present in the free amine. Thus, the 'stacked' forms may further be grouped in two classes – those in which the amino group is part of a rigid hydrogen-bridged network and those in which the amino group is relatively free. For compounds of the former class, the 'visible band' occurs at an appreciably lower energy than for compounds of the latter class – hence the purple-to-yellow color change. The fact that the yellow form of [$RhCl(CO)_2$(2-naphthylamine)] is less stable than the purple form and spontaneously changes to it in the presence of chlorinated solvents supports the conclusion that hydrogen bonding of the -NH_2 groups plays an important role in the stabilization of the dark-colored forms.

Conclusions

The present investigation has lead to an understanding of the structural differences between the two crystalline forms of the [$RhX(CO)_2$(Amine)] complexes, and also to a rationalization for their existence. In general, the 'stacked' species appear to be energetically favored over the 'non-stacked' ones, and the latter occur only when the steric requirements of the amine ligands effectively prevent interactions among adjacent rhodium(I) centers.

Examination of the some fifty complexes studied in this work points out that although color itself is not diagnostic of the structural type, the pattern of the electronic spectrum is; such a pattern can thus serve as a simple but effective tool in the identification of Rh(I) species involving metal–metal interactions of this type. The close similarity between the spectra of the many 'stacked' [$RhX(CO)_2$(Amine)] complexes investigated by us and that of [$PtCl_2$(ethylenediamine)] further suggests that this particular spectral pattern is relatively independent of both the metal system and the surrounding ligands, and may therefore be expected to occur in 'stacked' crystalline complexes of other d^8 metals such as Ni(II), Pd(II), Ir(I), and Au(III). It will be interesting to see, in the light of this suggestion, whether the existence of 'stacked' forms involving some degree of metal–metal interaction may not actually be more common than was previously recognized.

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