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Preparation and Analysis of ε-Caprolactam and ε-Thiocaprolactam Platinue(II) and Rhodium(III) Complexes

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The synthesis and properties of some Pt(II) and Rh(III) complexes with ε-caprolactam (L) and ε-thiocaprolactam (L') are reported. The compounds, L_3RhCl_3, L_2PtCl_2, $[L'_4RhCl_2]Cl$ and $[L'_4Pt]Cl_2$, have been characterized by chemical analysis, infra-red, n.m.r. and electronic spectra, X-ray powder diffraction and electrical conductance. Evidence is presented for coordination of the unidentate ligands through the oxygen or sulfur atoms. Configurational assignments indicate trans-coordination in both the square-planar L_2PtCl_2 and octahedral L_3RhCl_3 complexes.

Introduction

The present work is part of a research program in the field of catalysis over transition metals supported on polyamides. We have recently given evidence that the properties of these catalysts are related to the presence of specific surface complexes originating from the interaction of the transition metal (Rh, Pd, Pt) and reactive groups of the polyamide chain[1,2]. To gain further information, we have now attempted to synthesize analogous complexes using the monomer, ε-caprolactam, as ligand of the transition metals; no such complexes have previously been described in the literature, although several ε-caprolactam complexes with other metals are known[3–9]. The investigation was extended to include ε-thiocaprolactam, which has only once been employed as a ligand[10].

The present paper describes the synthesis and analysis of Pt(II) and Rh(III) complexes both with ε-caprolactam and ε-thiocaprolactam. These new compounds have been characterized by chemical analysis, infrared, n.m.r. and optical spectroscopy, X-ray powder diffraction and electrical conductance. Our findings lead to assign coordination to the central ions through oxygen or sulfur.

Experimental Section

Reagents

ε-Caprolactam (Montedison) was recrystallized from petroleum ether before use; m.p. = 70° C. ε-Thiocaprolactam was obtained from ε-caprolactam by reaction with P_2S_5[11] and recrystallization from *p*-xylene; m.p. = 105° C. $PtCl_2$ was obtained from $H_2PtCl_6 \cdot 6H_2O$ by reduction with $N_2H_4 \cdot 2HCl$[12]. $RhCl_3 \cdot 3H_2O$ (Schuchardt) was used without purification. All materials and solvents were of reagent-grade quality.

Preparation of Compounds

Trichlorotris(ε-caprolactam)rhodium(III), $[(C_6H_{11}NO)_3RhCl_3]$

A solution of $RhCl_3 \cdot 3H_2O$ (0.5 g) in absolute ethanol (15 ml) was added, under N_2, to ε-caprolactam (1.5 g) also dissolved in absolute ethanol (10 ml). A red precipitate was immediately formed which mostly disappeared after 20 h stirring to give a red solution. After filtration, the solvent was distilled off under reduced pressure; the residue was repeatedly washed with dry ether to remove excess of ε-caprolactam, recrystallized from absolute ethanol and dried under reduced pressure at room temperature. The pink compound, $(C_6H_{11}NO)_3RhCl_3$, is stable in air, soluble in acetone and ethanol, insoluble in ether and water. Yield: 82%. Found: C, 38.7; H, 5.9; N, 7.3; Cl, 19.3; Rh, 18.3. Calcd. for $C_{18}H_{33}N_3O_3RhCl_3$: C, 39.3; H, 6.0; N, 7.6; Cl, 19.3; Rh, 18.7%.

Dichlorobis(ε-caprolactam)platinum(II), $[(C_6H_{11}NO)_2PtCl_2]$

$PtCl_2$ (0.5 g) and ε-caprolactam (7 g) were heated to 75° C, and the melted mixture was stirred under

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TABLE I. Some Vibrational Frequencies of ε-Caprolactam and its Metal Complexes (Nujol, NaCl, 4000–750 cm^{-1}).

Compound	Vibration Mode (cm^{-1})			
	ν(C=O)	ν(N–H)	$\nu(N\text{–}H)_{ass}$	Other bands (cm^{-1})
L[a]	1660s	~3400	3280, 3210, 3080[b]	1658, 1314, ~820[c]
L_2PtCl_2	1615s		3170m	2900vs, 2840s, 1455vs, 1373s, 1360m, 1310w, 1195w, 1100w, 1082w, 1073w, 1020w, 980w, 965w, 872w, 840w, 819w
L_3RhCl_3	1620s		3270m–3198m	2900vs, 2830vs, 1498m, 1459s, 1432m, 1412m, 1370m, 1350m, 1333w, 1317w, 1287m, 1260w, 1233vw, 1197s, 1163w, 1112w, 1087m, 1019w, 980m, 965w, 893w, 870w, 850w, 826m

[a] L = ε-caprolactam. [b] Ref. 8. [c] Ref. 11. s, strong; m, medium; w, weak.

N_2 for 4 h. After cooling, the mixture was treated with dry acetone and, after filtering, the solvent was evaporated under reduced pressure. The residue was repeatedly washed with dry ether in a dry box under N_2 to remove excess ε-caprolactam and then dried under reduced pressure at room temperature. The brown product, $(C_6H_{11}NO)_2PtCl_2$, is freely soluble in dry acetone and absolute ethanol, insoluble in ether and decomposes in water. Yield: 57%. Found: C, 30.2; H, 4.5; N, 5.4; Cl, 14.1; Pt, 39.4. Calcd. for $C_{12}H_{22}N_2O_2PtCl_2$: C, 29.3; H, 4.5; N, 5.7; Cl, 14.4; Pt, 39.6%. Attempts to prepare the same complex using an ethanolic solution of ε-caprolactam or starting from K_2PtCl_4 instead of $PtCl_2$, were unsuccessful. Because of its instability, the electrolytic conductivity of the (ε-caprolactam)$_2$PtCl$_2$ complex was not determined.

Dichlorotetra(ε-thiocaprolactam)rhodium(III) chloride, $[(C_6H_{11}NS)_4RhCl_2]Cl$

A solution of $RhCl_3 \cdot 3H_2O$ (0.5 g) in ethanol (100 ml) was added to a solution of ε-thiocaprolactam (2.0 g) in benzene (100 ml), and the mixture was heated to reflux, with stirring, for 2 h. After cooling, the solution was reduced to a small volume (*ca.* 50 ml) under reduced pressure and then treated with ether (200 ml) to yield a yellow precipitate. The product was filtered, repeatedly washed with ether and recrystallized from water. The yellow crystalline compound is soluble in water and ethanol and insoluble in ether. Yield: 95%. Found: C, 38.8; H, 6.2; N, 7.7; S, 17.9; Cl, 14.2. Calcd. for $C_{24}H_{44}S_4N_4RhCl_3$: C, 39.8; H, 6.0; N, 7.7; S, 17.6; Cl, 14.6%.

Tetra(ε-thiocaprolactam)platinum(II) dichloride, $[(C_6H_{11}NS)_4Pt]Cl_2$

$PtCl_2$ (0.5 g) was added to ε-thiocaprolactam (1.2 g) dissolved in ethanol (100 ml). The mixture was refluxed for 2 h with stirring. After cooling and filtering, the solution was reduced to a small volume (*ca.* 50 ml) under reduced pressure. The resulting white precipitate was filtered, repeatedly washed with ether, and recrystallized from water. The product was soluble in water and ethanol and insoluble in ether. Yield: 85%. Found: C, 37.3; H, 5.0; N, 7.0; Cl, 8.9; S, 16.5. Calcd. for $C_{24}H_{44}N_4S_4PtCl_2$: C, 36.8; H, 5.7; N, 7.1; Cl, 9.1; S, 16.5%.

Physico-chemical Measurements and Analytical Procedures

Infrared spectra (Tables I–III) were taken on a Perkin–Elmer Model 225 recording spectrophotometer by using NaCl windows as Nujol mull smears in the 4000–650 cm^{-1} range and CsBr optics between 650 and 250 cm^{-1}; spectra were also run by KBr disk technique (300 mg of KBr mixed with *ca.* 1 mg of the substance).

Electronic spectra in the 210–700 nm region were obtained with a Perkin–Elmer EPS-3T recording spectrophotometer. Table IV summarizes the results.

The ^1H NMR spectra of the free ligands and the four complexes (Table V) were recorded on a Varian HA100 spectrometer operating at 100 MHz. ^{13}C NMR spectra (Table VI) were obtained from a Jeol PS-100 Fourier-transform spectrometer operating at room temperature and at 25.15 MHz with complete noise decoupling of the protons. All spectra were registered from $CDCl_3$ solutions and are referenced to tetramethylsilane considering the ^{13}C resonance of $CDCl_3$ at 76.9 p.p.m.

X-ray powder patterns (Table VII) were obtained with a Philips PW 1050/1130/1370 diffractometer set-up using CuKα radiation. As various batches of crystallization gave identical X-ray diagrams, it ap-

TABLE II. Absorption Frequencies in Far Infrared (750–200 cm^{-1}).[a]

Compound	δ_{NCO} - (cm^{-1})	$\nu_{M\text{–}Cl}^{as}$ (cm^{-1})	Other bands
L	690m	–	255w, 320m, 396m, 488s, 503s, 581s
L_3RhCl_3	731m	344s	235w, 258w, 330ms, 416w, 496w, 560m, 603m, 648m
L_2PtCl_2	718m	320m	376w, 510w, 602w, 676w

[a] ν, stretching; δ, bending.

pears that in all cases only one polymorphic form was present.

Electrolytic conductance measurements were performed with a Leeds–Northrup conductivity bridge

TABLE III. Some Vibrational Frequencies of ε-Thiocaprolactam and its Pt(II) and Rh(III) Complexes (Nujol, NaCl, 4000 to 200 cm^{-1}).

Compound			Vibration Mode[b]
L′[a]	$[L'_4Pt]Cl_2$	$[L'_4RhCl_2]Cl$	
(3410)[c]			ν(N–H)
3180s	3050m	3240m	$\nu(N\text{–}H)_{ass}$
		3140m	
2900s	2920s	2930s	$\nu(CH_2)$
	2858s	2858s	
1640w			
1540s	1560s	1580s	ν(CN) + δ (N–H)/B-band
1460m	1457s	1465m	$\delta(CH_2)$
1435m	1440sh	1441s	
1400m	1400m		$\omega(CH_2)$
1365ms	1373ms	1365ms	$\omega(CH_2)$
	1360m		
1343m	1351ms	1350m	ν(CN) + ν(CC)/C-band
1330m	1332m	1334m	
1310m	1320w	1320sh	
1288w		1292w	
1255m	1259m	1258w	
1230m	1237w	1240w	
1207m	1220m	1213s	$\gamma(CH_2)$
	1212w		
1170ms	1171s	1168s	
1110s	1110s	1105s	
1065s	1070s	1062s	$\nu(CNS)_{symm}$/D-band
1050sh	1062s	1050m	
998m	995m	995m	
980ms	978m	979s	
938m	936w	932w	
887m		887w	
845m	850m	842m	γ(N–H)
840m			
790s	805m	779m	γ(N–H)
778s	782m	760ms	
	720w	720m	
710m	710w	708m	
605m	608m	598mw	
532s	534w	529m	
	496w		
482s	490w	480m	
390vw		410vw	
362s		370w	
330vw	333w	321m	
310s		310w	
		277m	
250m		250w	

[a] L′ = ε-thiocaprolactam. s, strong; m, medium; w, weak; vw, very weak. [b] ν, stretching; δ, bending (in plane); γ, twisting; ω, wagging. [c] Not observed (see ref. 30).

TABLE IV. Electronic Spectra.

Compound[a]	Solvent	Absorption Maxima $\nu(cm^{-1})$[b]	ε_{max} (l mol^{-1} cm^{-1})
L_3RhCl_3	C_2H_5OH	20.620	180
		26.310	167
L_2PtCl_2	CH_3COCH_3	26.460	shoulder
		23.530	weak
$[L'_4RhCl_2]Cl$	C_2H_5OH	23.260	915
		(29.410)	shoulder
$[L'_4Pt]Cl_2$	C_2H_5OH	28.170	shoulder

[a] L = $C_6H_{11}NO$; L′ = $C_6H_{11}NS$. [b] All bands are rather broad.

TABLE V. Chemical Shifts (p.p.m. from TMS) of Proton Resonances (τ scale).

	L	L_2PtCl_2	L_3RhCl_3
Hα	7.6_0	7.4_0	7.4_0
Hβ,γ,δ	8.3_0	8.2_8	8.3_0
Hε	6.8_0	6.3_5	6.6_0
NH	3.0	3.4_5	–

	L′	$[L'_4Pt]Cl_2$	$[L'_4RhCl_2]Cl$
Hα	7.0_0	7.2_5	7.1_0
Hβ,γ,δ	8.3_0	8.3_5	8.3_0
Hε	6.6_0	6.3_5	6.3_5
NH	0.4_5	–2.0	–0.3, –0.7, –0.9

Nomenclature:

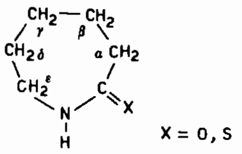
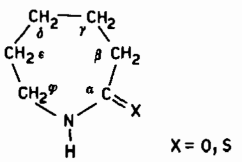


TABLE VI. Chemical Shifts (p.p.m. from TMS) of ^{13}C Resonances.

	L	L′	$[L'_4Pt]Cl_2$	$[L'_4RhCl_2]Cl$
Cα	179.8	209.9	197.5	200.0; 200.4; 202.3
Cβ	36.1	44.4	40.0	40.8
Cγ	22.5	23.7	23.7	23.8
Cδ	28.9	27.2	26.6	26.5
Cε	29.9	29.7	29.7	29.3
Cφ	41.9	46.4	46.8	47.8

Nomenclature:

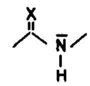


and a conventional cell previously calibrated with an aqueous solution of KCl. All measurements were made at 20° C, in nitromethane (Table VIII).

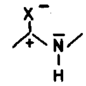
Rh and Pt analyses were carried out on an atomic absorption spectrophotometer (Perkin–Elmer Model 303); Cl and S analyses were obtained by a standard volumetric procedure[1]; lower atomic weight elements were determined on a Hewlett–Packard Model 185 C–H–N Analyzer.

Results and Discussion

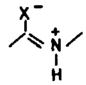
The electronic structure of ε-(thio)caprolactam is best described as a resonance hybrid of the main structures:



(1)



(2)



(3)

where X = O, S. As to the differences between amides and thioamides, we notice that the contributions of the canonical forms **(2)** and **(3)** are greater in the latter case, as a consequence of the higher polarizability of sulfur[14].

Since the complexes allow for two possible centres of coordination, either (O, S) or N, it is of interest to try to determine the site of coordination. In view of the good electron-donating properties of the ligands, metal coordination through (O, S) will lead to a decrease in the (thio)carbonyl stretching force and an increase of the C–N frequency. Coordination to nitrogen, on the other hand, would increase the contribution of structure **(1)** to the ground state of the complexes and cause an increase in the (thio)carbonyl frequency and decrease of CN and NH stretching frequencies[15,16]. The use of stretching vibrations for diagnostic purposes involving the metal atom appears less straightforward, as these are usually occurring in a rather wide frequency range and are often weak, as in the case of ν (Pt–N).

ε-Caprolactam Complexes

The reaction between ε-caprolactam (L) and the metal chloride, carried out as described in the Experimental section, yielded products that can be formulated

TABLE VII. Interplanar Spacings of ε-(thio)caprolactam Platinum(II) and Rhodium(III) Complexes.

L_2PtCl_2		$[L'_4Pt]Cl_2$		L_3RhCl_3		$[L'_4RhCl_2]Cl$	
d(Å)	I/I_o	*d*(Å)	I/I_o	*d*(Å)	I/I_o	*d*(Å)	I/I_o
10.88	7	9.56	100	11.55	15	13.02	$\geqslant$100
10.11	76	9.16	24	10.95	8	11.98	74
9.71	30	8.51	25	10.72	8	9.24	6
9.54	100	7.91	20	9.82	8	8.06	16
6.90	27	7.80	28	9.45	15	7.69	14
6.70	6	7.41	28	8.90	17	6.84	14
6.45	11	6.97	6	8.55	100	6.57	70
6.18	25	6.31	16	8.16	10	6.32	21
5.76	20	5.76	1	7.80	23	6.04	4
5.60	64	5.33	5	7.54	36	5.84	9
5.44	15	5.26	6	7.25	26	5.73	3
5.32	60	5.23	7	6.81	15	5.58	12
5.16	32	5.08	13	6.51	10	4.99	7
4.91	7	4.88	31	6.37	17	4.62	49
4.86	15	4.84	22	6.14	11	4.54	15
4.76	21	4.62	7	6.03	7	4.39	11
4.62	24	4.58	13	5.78	22	4.15	7
4.46	42	4.51	9	5.73	32	4.04	4
4.40	13	4.36	15	5.49	15	3.96	2
4.31	6	4.28	3	5.38	10	3.87	10
4.22	13	4.13	5	5.20	7	3.64	6
4.05	31	4.09	3	5.10	6	3.55	19
4.00	11	4.05	2	4.96	24	3.45	5
3.84	11	3.97	2	4.84	9	3.38	5
3.58	5	3.91	1	4.81	16	3.05	2
3.52	22	3.82	2	4.77	33	2.931	6
3.45	7	3.77	1	4.69	22	2.902	4
3.43	6	3.71	12	4.53	6	2.866	9
3.35	3	3.61	10	4.49	12	2.857	8

TABLE VII. (Cont.)

L_2PtCl_2		$[L'_4Pt]Cl_2$		L_3RhCl_3		$[L'_4RhCl_2]Cl$	
d(Å)	I/I_o	*d*(Å)	I/I_o	*d*(Å)	I/I_o	*d*(Å)	I/I_o
3.29	22	3.57	5	4.45	5	2.840	7
3.23	9	3.48	1	4.38	10	2.733	3
3.17	5	3.44	3	4.31	6	2.641	10
3.14	9	3.33	7	4.21	6	2.584	7
3.04	15	3.31	4	4.16	13	2.549	5
2.875	7	3.24	3	3.97	17	2.488	10
2.845	15	3.16	6	3.91	16	2.432	6
2.814	18	3.14	3	3.85	11	2.391	2
2.662	11	3.04	5	3.78	6	2.369	3
2.617	9	2.981	2	3.62	4	2.309	2
2.554	6	2.930	5	3.57	8	2.271	5
2.489	5	2.888	3	3.44	8	2.221	2
2.459	3	2.847	2	3.31	8	2.201	6
2.370	9	2.826	5	3.25	5	2.168	3
2.349	12	2.752	3	3.17	4	2.101	4
2.314	12	2.681	2	3.12	7	2.012	4
2.233	11	2.637	3	2.92	8	1.979	2
2.167	6	2.613	7			1.939	2
2.145	6	2.598	4			1.870	3
2.108	5	2.567	6			1.774	5
2.095	5	2.556	5				
2.050	5	2.545	6				
2.020	6	2.498	5				
1.982	5	2.488	6				
1.966	5	2.445	4				
1.921	7	2.408	3				
1.875	5	2.394	2				
		2.343	4				
		2.319	2				
		2.309	3				
		2.298	2				
		2.268	2				
		2.093	3				
		2.067	5				
		2.049	3				
		2.032	4				
		2.025	4				
		1.914	4				
		1.908	4				
		1.889	3				
		1.858	2				
		1.744	2				
		1.722	4				

TABLE VIII. Electrolytic Conductivities at 20° C in Nitromethane.

Compound	Concentration (m*M*)	λ_m (ohm^{-1} cm^{2}mole^{-1})	Ionic Nature
L_3RhCl_3	3.00	3.5	–
L_2PtCl_2	n.d.	n.d.	–
$[L'_4RhCl_2]Cl$	3.00	72.6	1 : 1
$[L'_4Pt]Cl_2$	3.00	171.0	1 : 2

as non-ionic complexes L_2PtCl_2 and L_3RhCl_3, on the basis of their elemental analysis, solubilities and conductivity measurements (Table VIII). They are very similar to L_2NiCl_2 and L_3CuCl_2[4] and to the metallic complexes reported for N,N′-dimethylformamide[13]. On the grounds of their stoichiometry and in view of established geometries of analogous compounds, it is reasonable to expect that the Pt(II) and Rh(III) complexes exhibit a planar and an octahedral coordination, respectively. The platinum complex is very sensitive to moisture, while the rhodium one is much more stable.

Infrared spectra of the complexes were recorded to determine the coordination site. Since the spectrum of the free ligand ε-caprolactam itself has been analyzed[11], band shifts caused by coordination can be checked immediately. The ε-caprolactam complexes appear to be coordinated to the metal by the oxygen atom as the C=O frequency in the i.r. spectra is shifted to lower frequencies with respect to that of the free ligand; the shift amounts to about 40 cm^{-1} and is comparable to other cases reported in the literature[13,17]. Although coupling with the CH_2 bending vibrations prevents evaluation of the variations in the CN frequencies, the results obtained are confirmed by the shifts in the N–C–O bending ($\Delta\nu \approx +40$ cm^{-1}). The binding situation thus corresponds to the normal findings for ε-caprolactam complexes[4,8,9]; only in the case of $[Pt(urea)_2Cl_2]$ nitrogen-to-metal bonds have been established[16]. Complexing at the oxygen site also affects the N–H stretching frequency, as is obvious from the resonance structures. Interpretation of the observed frequencies is complicated here by the associative tendency of the free ligands. The presence of any metal–nitrogen skeletal vibrations is also ruled out by comparison with bis(ethylenediamine)platinum(II) halides[18]. Observation of the visible spectrum of L_2PtCl_2 with the spectrochemical effects in other square-planar Pt(II) complexes (Table IX) confirms the presence of $PtCl_2O_2$ chromophores.

Examination of the far-infrared region in the spectrum of L_2PtCl_2 reveals only one active metal–chlorine stretching vibration, a feature which agrees with the symmetry requirements of a *trans*-L_2PtCl_2 complex; the frequency of 320 cm^{-1} falls in the generally accepted ν(Pt–Cl) range.[19–24] This *trans*-coordination is also expected on the basis of stereochemical considerations.

L_3RhCl_3 shows an electronic (reflectance) spectrum corresponding to the expectations for an octahedral rhodium(III) complex, as it shows two broad *d–d* absorption bands at about 400 and 500 nm, *i.e.* in the wavelength range expected for the $RhCl_3O_3$ chromophore (compare absorptions of $RhCl_3(DMF)_3$ [13]at 390–406 nm and 492–508 nm with those of $RhCl_3$ $(pyridine)_3$ at 360–370 nm and 425–450 nm[25]. In case of trichlorotris(ε-caprolactam)rhodium geometric isomerism is further possible, as it has been observed for other L_3RhCl_3 structures (L = NH_3, RNH_2, py, thu, ethyleneimine)[25–27]. Diagnosis of the stereochemistry is made on the basis of the Rh–Cl frequencies in the 400–200 cm^{-1} range. The observed medium absorption in the range 258 to 235 cm^{-1} and the strong band at 344 cm^{-1} appear to conform to *trans*-L_3RhCl_3, which group-theoretical predictions attribute to three infra-red active Rh–Cl modes ($2a_1+b_1$) due to C_{2v} point symmetry. The strong 344 cm^{-1} band corresponds to the antisymmetric b_1 mode, involving the *trans*-chlorine atoms in the octahedral Rh(III) complex[22].

TABLE IX. Spectrochemical Effects in Square-planar Pt(II) Complexes.

Complex[a]	Coordination of Pt(II)	First Allowed *d–d* Transition (nm)	Ref.
$[PtCl_4]^{2-}$	4 Cl	389	35
L_2PtCl_2	2 Cl + 2 O	378[b]	Present work
$PtCl_2(DMF)_2$	2 Cl + 2 O	360–365[c]	13
$[PtCl_3NH_3]^-$	3 Cl + 1 N	346	36
$[Pt(NH_3)_4]^{2+}$	4 N	244	36

[a] L = ε-caprolactam. [b] Weak band at 425 nm. [c] Weak bands at 450 nm and 670 nm.

ε-Thiocaprolactam Complexes

The previously described reaction between ε-thiocaprolactam and platinum or rhodium chlorides yielded stable products that on the basis of their analytical data, solubilities and conductivity measurements can be formulated as ionic complexes: $[L'_4Pt]Cl_2$ and $[L'_4RhCl_2]Cl$. In fact, they are soluble in polar solvents and their molar conductivities (Table VIII) indicate an ionic structure.

Attempts to establish the coordination sites of the ligands are again based on infrared data. Unfortunately substitution of oxygen for sulfur changes so completely the i.r. spectrum that it is usually very difficult to obtain much useful information from a comparison of the spectra of the thioamides with those of amides[28]. The band frequency assignments of ε-thiocaprolactam have first been reported by Mecke and Mecke[11]. Because of the strong vibrational coupling being present in the cyclic system, location of the characteristic thioamide bands is not unequivocal. The assignments reported in Table III agree with those proposed by Jensen and Nielsen[28]. From a spectroscopic point of view, complex formation does not radically change the nature of the interacting species and the corresponding frequencies of the complexes were easy to identify since they were not markedly shifted in position (in most cases only about 10 cm^{-1}).

As to the B- and C-amide bands at 1540 and 1330 cm^{-1} in the free ligand, we notice an increase in frequency. Especially the thioamide B-band[28] is very sensitive to complex formation. The shift towards higher frequencies in the complexes is explained by the increased double-bond character of the C–N bond following S-coordination. We notice that $[L''_4Pt]Cl_2$ complexes (L'' = thiourea, thioacetamide) are S-bonded[29] and that sulfur coordination is also reported for the other crystalline coordination compounds of ε-thiocaprolactam (L'): $[L'_2CoX_2]$ (X = Cl, Br, I) and $[L'_4Co]$ $(ClO_4)_2$[10]. Further conclusive evidence for S-coordination based on i.r. data was not obtained. Indeed, even though a major contribution to the D-band appears to be the symmetrical stretching vibration of the N–C–S grouping, coordination will affect the C–N and C–S bonds in an opposite way and the net frequency shift (either positive or negative) is therefore much smaller than for the B-band. Further, although it seems fully substantiated that the thioamide G-band, associated with the ν(CS) vibration, is normally found in the range cited for the single C–S stretching vibration (600–800 cm^{-1})[28] rather than near 1100 cm^{-1} [11], in our case this band could not be located with certainty. Furthermore, as in case of ε-caprolactam complexes, confidence in the observed trends of the high N–H stretching frequencies is limited by the association tendency of the free ligand[30].

Thus, at variance with the conclusive i.r. information concerning the coordination of the ε-caprolactam complexes, some uncertainty exists in the case of the thio-analogues. The ^1H NMR spectra (Table V) also do not provide more definite information. In first approximation one would expect the hydrogens nearest to the coordination site to be the most sensitive. In fact, the hydrogens of the β, γ, δ methylenes are practically not shifted, but the α and ε methylenic hydrogens are almost equally shifted. In the ε-caprolactam complexes the α and ε methylenes are both to lower field, whereas the α and ε hydrogens of the ε-thiocaprolactam complexes have the resonance to the higher and lower field respectively. It is difficult to correlate the direction of the shift with the coordination site as the anisotropies of the $-\underset{\underset{\displaystyle O}{\|}}{C}-NH-$ and $-\underset{\underset{\displaystyle S}{\|}}{C}-NH-$ groups are too complex[31] for a reliable prevision of the influence of the coordination site. Also, the NH shifts are ambiguous as they strongly depend on the concentration.

More conclusive evidence for the ε-thiocaprolactam complexes was obtained by means of ^{13}C NMR spectra (Table VI). The ε-caprolactam ^{13}C magnetic resonance spectrum is well known and has already been analysed[32]. On this basis we have assigned the ^{13}C signals of the other compounds as reported in the table. The spectra of the two complexes look very similar and in favour of the same donor group, most likely the sulfur atom. The result is then that the α and β carbon signals shift to higher field. Coordination to the nitrogen atom would have induced a measurable shift of the φ carbon. The other carbon atoms are practically unaffected. Finally, we note that the thiocarbonyl in the complex $[L'_4RhCl_2]Cl$ presents three signals (note also the three signals from the NH group in Table V), probably related to the isomeric structural possibilities. No evidence of spin coupling Rh–X–C, Pt–X–C has been noted.

At variance with the corresponding tetrahedral $[L'_4Co]^{2+}$ ions[10], $[L'_4Pt]Cl_2$ probably contains cations with Pt in square pyramidal ε-thiocaprolactam coordination. Although the uncertainties in the assignments of the vibrations do not allow definitive conclusions with regard to the inner structure of the dichlorotetra-(ε-thiocaprolactam)rhodium cation, we notice that other octahedral complexes of the type $[L''_4RhCl_2]$ Cl or $[L'''_2RhCl_2]Cl$ (L'' = NH_3, py, L''' = bipy, phen) are all *trans* (*cf.* ref. 27, 33, 34).

Conclusions

L_2PtCl_2 and L_3RhCl_3 (L = ε-caprolactam) are non-ionic compounds which exhibit complexing at the oxygen site and *trans* coordination of the ligands with square-planar and octahedral geometry, respectively. Similarly, the ionic $[L'_4Pt]Cl_2$ and $[L'_4RhCl_2]Cl$ complexes, where L′ = ε-thiocaprolactam, coordinate at the sulfur site.

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