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Platinum Carbonyl Complexes

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The synthesis, characterization and i.r. spectra of platinum(II) carbonyl complexes with bridging ethylenediamine and its N–alkyl derivatives having the formula, $(Pt(CO)X^2)_2en$*, where* $en = H_2NCH_2CH_2NH_2$ *and* $X = Cl, Br$ *are described.*

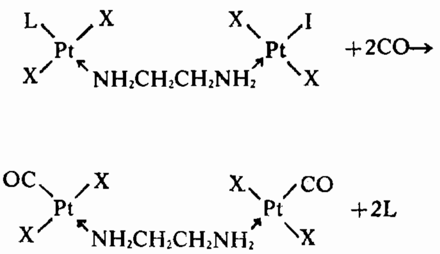
Introduction

Platinum carbonyl complexes are the oldest metal carbonyl compounds. P. Schützenberger[1] one hundred years ago first reported platinum carbonyl complexes and the reaction of ammonia with the dichloro platinum(II) carbonyl, $Pt(CO)_2Cl_2$. Synthesis and infrared studies have been reported,[2,3a,b] and recently Orchin and his co-workers have described olefin and carbonyl platinum complexes and examined their i.r. and n.m.r. spectra.[3c]

In the present paper the synthesis of bridging dinuclear carbonyl compounds and their reactions and infrared spectra are reported. The infrared spectra of the dinuclear compounds can be interpreted in terms of simpler monomers characteristic of the units from which they are built up. For instance, the i.r. spectrum of $(CO)X_2Pt(NH_2CH_2CH_2NH_2)PtX_2(CO)$ is made up of two equivalent units of $PtX_2(CO)$ and ethylenediamine. We will discuss the i.r. spectra and the structures of ethylenediamine bridging compounds by comparing them with simpler analogs of platinum carbonyl compounds, such as $[PtCl_3(CO)]^-$ and *cis-* or *trans*–$[PtCl_2(NH_3)(CO)]$.[4,5,6] The spectra are interpreted in terms of ethylenediamine and PtX_2CO units separately, or as $Pt(NH_2CH_2CH_2NH_2)Pt$ and $PtX_2(CO)$ units.

Results and Discussion

The dinuclear carbonyl complexes are obtained by reacting the analogous platinum(II) acetylene[7] or ethylene[8] complexes with carbon monoxide, according to the following reaction:



(1)

where, $L = (CH_3)_2C(OH)C{\equiv}CC(OH)(CH_3)_2$ or C_2H_4 and the bridge is either ethylenediamine and its derivatives or 4,4–dipyridyl.

The new compounds are obtained in high yields (80%).

The complexes are stable thermally, but quickly decompose in water. They are soluble in acetone, tetrahydrofuran and alcohol, but decompose slightly on standing.

Reaction (1) is taking place in anhydrous ether. $(PtLX_2)_2en$ (1 to 2 mmoles) in 80 ml ether at room temperature is stirred, and carbon monoxide is bubbled through the solution. The complexes then are washed with dry ether and dried over P_2O_5.

The infrared spectra of the compounds support a *trans*-configuration for ethylenediamine in the complexes with a C_{2h} symmetry.[9] Similar results were obtained for the complexes: $(Pt(C_2H_4)Cl_2)_2en$,[10] $[Hg(en)Cl_2]_\infty$,[11] and $Cd(en)M'(CN)_4 . 2C_6H_6$,[12] where M′ = Ni, Pd. A survey i.r. spectrum of the chloro-derivative, $(Pt(CO)Cl_2)_2en$ is shown in Figure 1. The i.r. spectra are simple and the bands are assigned separately to the ethylenediamine molecule and the unit $PtCl_2CO$ (see Table I). The assignments are made on the basis of i.r. spectra, and on Raman spectra of

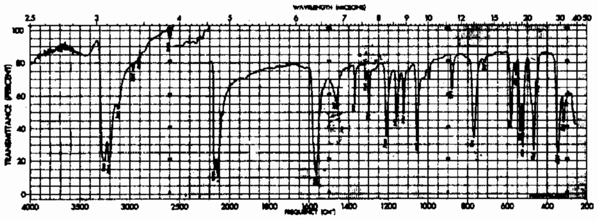


Figure 1. Survey i.r. spectrum of $(Pt(CO)Cl_2en$.

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Table I. i.r. Foundamental bands and assignments of $(Pt(COCl_2))_2en$.

	Number	Species	Frequency in cm^{-1}	Assignment
	ν_1	Au	3200vs (1.36)	NH_2 sym. str.
	ν_2		2921vw	CH_2 asym. str.
	ν_3		1312w	CH_2 twist.
	ν_4		1206s (1.35)	NH_2 twist.
	ν_5		877m	CH_2 rock.
	ν_6		687 (1.37)	NH_2 rock
Pt(en)Pt	ν_7		475m	C-N trs.
trans-ethylenediamine	ν_8		174m	C-C trs.
total modes:	ν_9	Bu	3245vs (1.34)	NH_2 asym. str.
$14\times3-6=36$	ν_{10}		2964w	CH_2 sym. str.
i.r. active, 18	ν_{11}		1563vs (1.34)	NH_2 bend.
(8Au+10Bu)	ν_{12}		1464m	CH_2 bend.
	ν_{13}		1367m	CH_2 wag.
	ν_{14}		1296m (1.32)	NH_2 wag.
	ν_{15}		1053vs	CN str.
	ν_{16}		516m	$^{\nu}$Pt-N
	ν_{17}			PtNC bend.
	ν_{18}		475	NCC bend.
$PtCl_2CO$ unit	ν_{19}	Au	318m	Pt-Cl sym. str.
à$2PtCl_2CO$	ν_{20}		197vs	Cl Pt Cl bend.
total modes $10\times3-6=24$	ν_{21}			N Pt Cl bend.
i.r. active 12	ν_{22}		213m	C Pt Cl bend.
(5Au+7 Bu)	ν_{23}		516m (1.03)	Pt-N str.
	ν_{24}	Bu	536s	Pt-C str.
	ν_{25}		2144vs	$C\equiv O$ str.
	ν_{26}		495s	PtCO bend.
	ν_{27}		344vs	Pt-Cl asym. str.
	ν_{28}		253m	NPtCl bend.
	ν_{29}		220sh	NPtC bend.
	ν_{30}		288m	CPtCl bend.

trs = torsion

Table II. Characteristic infrared band assignments in the region 600-200 cm^{-1}.

Compound	ν_{Pt-C}	ν_{Pt-N}	δ_{Pt-CO}		ν_{Pt-Cl}	ν_{Pt-Br}
$((CO)PtCl_2)_2$ en	536ms	516m	466s,450w		344s,318m	
$((CO)PtCl_2)_2$ en*	535s	520s	465s,450m		350vs,317s	
$((CO)PtCl_2)_2$ en D_4	536s	507m	475m,445s		348s,317m	
$((CO)PtBr_2)_2$ en	549m	519s	465vs,455sh			245s,225ms
$((CO)PtCl_2)_4$ en $H_2(CH_3)_2$	530s	515m	476s,443m		346vs,315s	
$((CO)PtCl_2)_2$ en $D_2(CH_3)_2$	530s	506m	476s,440m		347vs,315s	
$((CO)PtCl_2$ en$(CH_3)_4$	542s	520m,505m	490m,468m		344vs,338vs	
$((CO)PtCl_2)_2$ 4,4-dipy	542s	503m	463s		360vs,334s	
Pt(CO)Cl(8-hydroxyquinolinato)	551s	505m	474m	400(Pt-O)	350vs,330s	

* spectrum taken at 90°K.

the $[PtCl_3(CO)]^-$ ion reported by Denning and Ware.[4] The assignments are also supported by an approximate force constants calculation[6] of the mononuclear complex *trans*–$[PtCl_2(CO)NH_3]$.

The bridging complexes $(PtX_2(CO))_2en$ have $22\times3-6=60$ fundamental vibrations (18 Ag+12 Bg+13 Au+17 Bu) of which only 30 are i.r. active (13 Au+17 Bu)). Ethylenediamine alone has $12\times3-6=30$ fundamental vibrations and in the *trans*-isomer only 15 vibrations are active in infrared (7 Au+8 Bu). The two $(PtX_2(CO))_2$ units have $10\times3-6=24$ fundamental vibrations with twelve i.r. active (5 Au+7Bu). By coordination of the ethylenediamine molecule with the PtX_2CO units six new vibrations are formed of which only three are i.r. active (Au+2 Bu), ν_{16}, ν_{17}, ν_{18}.

The ethylenediamine molecule could also be considered as being attached to two metal atoms[12] with 36 fundamental vibrations (18 i.r. active) and two units $2(PtX_2CO)$ with 24 fundamental vibrations of which twelve are i.r. active (see Table I).

The characteristic group frequencies for these complexes in the low frequency region are given in Table II. Stretching frequencies for Pt–C, Pt–N, Pt–Cl, and Pt–Br are given. The assignment of platinum-carbon stretching and platinum-carbon bending vibrations agree with those of Denning and Ware.[4]

The high $\nu(C\equiv O)$ and the sharp decrease of δPtCO in the anion $[Pt(CO)Cl_3]^-$ have been explained[4] as being consistent with a greater contribution of the valence form $Pt-C\equiv O$ over the resonance form $Pt=C=O$. The high oxidation state of platinum (Pt^{2+}) favors a stronger σ bond and the negative charge does not tend to be redistributed to the π^* orbitals of CO *via* π back donation. This is consistent with the high ν(CO) and the lowering of δPtCO. The high

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(10) D.B. Powell and N. Sheppard, *J. Chem. Soc.*, 3089 (1959).
(11) K. Brodersen, *Z. anorg. und allgem. chem.*, *298*, 142 (1959).
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ν(Pt–C) is also in agreement with results of normal coordinate calculations[6] on *trans*–Pt(CO)(NH_3)Cl_2 in which the force constant of Pt–C bond is found to be 3.8×10^5 dyne/cm.

Gribov and co-workers[5] have calculated a Pt–C bond force constant of 3.5×10^5 dyne/cm in the same molecule, but they rejected this value, because it appeared improbable at that time, due to the high frequency of ν(CO). Borine carbonyl[13] H_3BCO, with only a σ bond shows a higher ν(CO) frequency than the free carbuyl[14] molecule (CO:2143 cm^{-1}, H_3BCO: 2166 cm^{-1}) indicating that the effect of σ donor alone increases the ν(CO).

The assignfiments of Pt–N stretching, NPtC and NPtCl bending modes are in agreement with the results of Denning and Ware and they are supported by the deuteration of the amino groups. The ClPtCl bending mode was confirmed by comparing the spectra of the chloro and bromo derivatives.

The $\nu C\equiv O$) absorptions are easily identified in the 2100 cm^{-1} region (see Figure 1 and Table III). In Table I only the high frequency band is reported for ν(CO).

The infrared spectra of the solid complexes show two strong and two weak bands in the region 2100 cm^{-1} (see Table III). The weak bands may be due to ^{13}CO stretching modes shifted by 50-35 cm^{-1} to lower frequencies from the strongest fundamental band. The crystal splitting of the strong carbonyl band is not shown in chloroform or carbon tetrachloride solutions for the Pt(CO)Cl (8–hydroxyquinolinato) complex, prepared by the same method (1) from Pt(C_2H_4)Cl(8–hydroxyquinolinato). One strong band is observed in this case accompanied by the weak ^{13}CO absorption. This presumably indicates that the splitting is due to crystal effects.

Table III. The infrared ν(CO) absorptions of the complexes in the solid state.

Compound [a]	Frequency cm^{-1} $\nu_{C=O}$	
(Pt(CO)Cl_2)$_2$en	2144 vs	
	2109 vs	
	2093 vw	
	2067 w	
(Pt(CO)Cl_2)$_2$enH_2Me_2	2133 vs	
	2123 vs	
(Pt(CO)Cl_2)$_2$en Me$_4$	2124 vs	
	2099 vs	
	2045 w	
(Pt(CO)Br_2)$_2$en	2059 w	
	2108 vs	
	2059 w	
(Pt(CO)Cl_2)$_2$4,4-dipy	2148 vs	
	2084 w	
(Pt(CO)Cl(8-hydroxyquinolinato)	2142 vs	2125 vs [b]
	2110 vs	
	2108 vw	
	2062 vw	2076 vw [b]

[a] en: $NH_2(CH_2)_2NH_2$, en H_2Me_2: $CH_3HN(CH_2)_2NHCH_3$, enMe$_4$: $(CH_3)_2N(CH_2)_2N(CH_3)_2$. [b] in $CHCl_3$ or CCl_4 two bands only were observed. s: strong, vs: very strong, m: medium, w: weak, vw: very weak.

Decomposition of the Complexes. The dinuclear carbonyl complexes hydrolyse in a similar manner to mononuclear and halogen-bridging complexes:

$$Pt(CO)Cl_3^- + H_2O = CO_2 + 2HCl + Pt + Cl^-$$

$$(Pt(CO)Cl_2)_2 + 2H_2O = 2CO_2 + 4HCl + 2Pt$$

$$(Pt(CO)Cl_2)_2en + 2H_2O = 2CO_2 + 4HCl + 2Pt + en$$

Hydrolysis is prevented by the addition of chloride ions to the solutions. The reactions of decomposition by heat are complicated. During the thermal decomposition there is liberation of carbon monoxide and carbon dioxide, in various relative amounts depending on the temperature.[3a] It is difficult to compare the Pt–C and Pt–N bond strengths. However, carbon monoxide is liberated first during decomposition followed by ethelenediamine. These species have been detected by i.r. spectroscopy in the gas phase after decomposition, carbon monoxide being observed first.

The complexes all decomposed sharlpy and lost carbon monoxide. The chloro-complexes are not thermally more stable than the corresponding bromo-complexes, as it is in the case with the halogeno-carbonyl complexes.[3a,15]

Methyl iodide, CH_3I did not react at all with the complexes in alcohol or acetone solutions at room temperature.

Experimental Section

The infrared spectra in the region 4000-200 cm^{-1} were obtained in Nujol mulls in KBr or CsI discs with a Perkin-Elmer 621 Spectrometer calibrated with a polystyrene film, CO_2 and H_2O vapors. The region 250-50 cm^{-1} was examined with a Berkman IR 11 spectrometer. Microanalyses were carried out by Dr. C. Daesslé, Montréal, Québec, Canada.

Bis(carbonyl)tetrachloro–μ–ethylenediamine platinate(II). $Cl_2(CO)Pt(NH_2(CH_2)_2NH_2)Pt(CO)Cl_2$. 0.2 g of (Pt(ac)$Cl_2$)$_2$en (7) were ground and added to anhydrous ether (80 ml). The suspension was agitated with a high speed magnetic stirrer at room temperature. Carbon monoxide gas was bubbled through the suspension until the solution became colorless (about forty minutes). The solution was then filtered, evaporated to dryness and the residue was washed with ether to yield a yellow-greenish powder. Melting point with decomposition 220°C.

Analysis Calcd. for $Cl_2(CO)Pt(NH_2(CH_2)_2NH_2)Pt(CO)Cl_2$: C, 7.41; H, 1.23; N, 4.32; Pt, 60.19. Found: C, 7.97; H, 1.70; N, 4.80; Pt, 58.80.

Bis(carbonyl)tetrachloro–μ–N,N′–dimethylenediamine–platinate(II), $Cl_2(CO)Pt(NHCH_3(CH_2)_2CH_3HN)$-$Pt(CO)Cl_2$. The compound was prepared as above from (Pt(ac)Cl_2)$_2$enH_2Me_2. Yellow crystals were obtained which melted with decomposition at 170°C.

Analysis. Calcd for: $Cl_2(CO)Pt(NHCH_3(CH_2(CH_2)_2$-$HN)PtCOCl_2$: C, 10.16; H, 1.77; N, 4.14; Pt, 57.60. Found: C, 10.37; H, 1.92; N, 4.01; Pt, 57.75.

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(13) George W. Bethke and M. Kent Wilson, *J. Chem. Phys.*, *26*, 1118 (1957).

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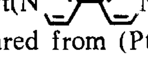
Bis(carbonyl)tetrachloro–μ–N,N′,N,N′–tetramethylenediamineplatinate(II), $Cl_2(CO)Pt(N(CH_3)_2(CH_2)_2N(CH_3)_2Pt(CO)Cl_2$. The compound was prepared from $(Pt(ac)Cl_2)_2enMe_4$. Light yellow crystals were obtained which decomposed at 144°C.

Analysis Calcd for $Cl_2(CO)Pt(CH_3)_2N(CH_2)_2(CH_3)_2)$-$Pt(CO)Cl_2$: C, 13.64; H, 2.27; N, 3.98; Cl, 20.17; Pt, 55.40. Found: C, 13.97; H, 2.59; N, 4.11; Cl, 19.95; Pt, 55.40.

Bis(carbonyl)tetrabromo–μ–ethylenediamineplatinate(II), $Br_2(CO)Pt(NH_2(CH_2)_2NH_2)Pt(CO)Br_2$. This compound was prepared from $(Pt(ac)Br_2)_2en$. Yellow crystals. Melting point with decomposition 190°C.

Analysis Calcd for $Br_2(CO)Pt(NH_2(CH_2)_2NH_2)Pt$-$(CO)Br_2$: C, 5.81; H, 0.97; N, 3.39; Br, 38.70; Pt, 47.22. Found: C, 6.10; H, 1.21; N, 3.36; Br, 39.10; Pt, 47.13.

Bis(carbonyl)tetrachloro–μ–4,4–dipyridylplatinate(II), $Cl_2(CO)Pt(N$$N)Pt(CO)Cl_2$. The complex was prepared from $(Pt(C_2H_4)Cl_2)_2(4',4'$–dipy) using the above method of bubbling carbon monoxide through a suspension of the platinum ethelene complex in ether. The $(Pt(C_2H_4)Cl)_2(4,4'$–dipy) complex was prepared from Zeise's salt. A solution of $K[Pt(C_2H_4)Cl_3]$, 0.3-0.5 g in 10 ml cold water was first prepared. To this solution 4,4′–dipy was added dropwise and by stirring the solution. A yellow precipitate was immediately formed. This was washed with cold water and dried over $CaCl_2$ in a desiccator under vacuum. The analysis for platinum and chlorine was correct.

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