Contribution from the Department of Chemistry,
Indian Institute of Technology, Madras-36, India

Cysteine Complexes of Palladium(II) and Platinum(II)

M. Chandrasekharan, M.R. Udupa, and G. Aravamudan

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Isolation of bis(cysteinato)palladium(II) and bis(cysteinato)platinum(II) is reported and their spectral characteristics have been examined. Both the complexes were square planar with the sulphur and oxygen atoms of the ligand being coordinated to the metal.

Introduction

Aminoacids which are important in the protein metabolism have been studied regarding their complexation with several biologically important metal ions. These acids easily function as chelating agents due to the presence of amino and carboxylate groups. Recently, Shindo and Brown[1] have studied the complexation of cysteine, $HSCH_2CH(NH_2)COOH$, (L), which has potentially three different atom types for coordination, with Zn^{II}, Cd^{II} and Hg^{II}. Complexation of Pt^{II} and Pd^{II} with glycine, DL-methionine and S-methyl-L-cysteine was reported,[2-4] in addition to the complexation with several first transition metal ions.[5] We report here the isolation and characterisation of bis(cyseinato)palladium(II) and bis(cysteinato)-platinum(II).

Experimental Section

Preparlation. Bis(cysteinato)palladium(II), [Pd-$(L\text{-}H)_2$]: K_2PdCl_4 (0.984 g, 3 mmole) in water (10 ml) was treated with 1*N* aqueous NaOH to give a brown precipitate of $Pd(OH)_2$. This was centrifuged, washed with water till free of sodium ions and added to a solution of cysteine hydrochloride monohydrate (2.1 g, 12 mmole) in water (10 ml), whose pH was previously adjusted to be between 6-7. The deep brown solution obtained was digested over a steam bath for about half an hour. The orange precipitate separated out was filtered, washed with methanol and ether and then dried in a vacuum desiccator. Bis(cysteinato)platinum(II), [$Pt(L\text{-}H)_2$]: K_2PtCl_4 (1.24 g, 3 mmole) in 25 ml water was added to cysteine hydrochloride monohydrate solution (2.1 g, 12 mmole) in water (10 ml). The pH of the whole solution was then adjusted to 6-7 by dropwise addition of dilute NaOH. The resultant yellow solution was kept over the steam bath for half an hour; the yellow precipitate obtained was filtered, washed with methanol and ether and dried in a vacuum desiccator. Analytical data of the complexes are given in Table I.

Physical Measlurements. The conductance measurement of $Pd(L\text{-}H)_2$ in conductivity water was made on a Philips 2209 conductivity bridge at 30°C. Ion-exchange experiments were made using columns (20 × 1 cm) of Amberlite IR 120, cationic and Dowex 1-Xl, anionic resins. Ultraviolet and visible spectral measurements were made for an aqueous solution of $Pd(L\text{-}H)_2$ using a Carl Zeiss DMR 21 recording spectrophotometer and the spectrum is reproduced in Figure 1. The measurements could not be undertaken for the platinum analogue owing to its insolubility in all common solvents. The magnetic measurements were carried out by the Gouy Method at room temperature. IR spectra were recorded by KBr pellet and nujol mull techniques for both $Pd(L\text{-}H)_2$ and $Pt(L\text{-}H)_2$ on a Perkin Elmer 257 Spectrophotometer in the range 625-4000 cm^{-1}. The characteristic i.r. frequencies are given in Table II and the spectra reproduced in Figure 2. IR spectra of the complexes in the range 200-650 cm^{-1} were recorded on a Beckman IR 12 spectrophotometer. The samples were made using nujol as mulling agent and pressed between polyethylene plates. Thermal analysis of the complexes was carried out on a Stanton recording thermobalance in air at a linear rate of heating of 6°/min using mullite crucible as container.

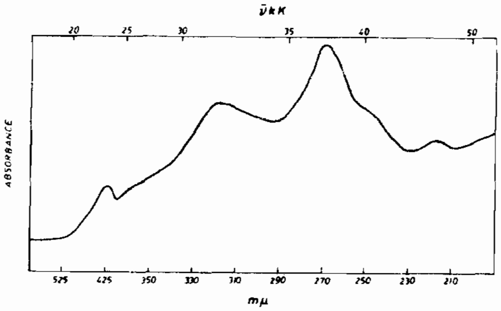

Figure 1. Electronic Spectrum of $Pd(L\text{-}H)_2$.

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(1) H. Shindo and L. Brown, *J. Am. Chem. Soc.*, *87*, 1905 (1965).
(2) S.E. Livingstone and J.D. Nolan, *Inorg. Chem.*, *7*, 1447 (1968).
(3) K. Nakamato, *J. Am. Chem. Soc.*, *83*, 4528 (1961).
(4) C.A. McAuliffe, *J. Chem. Soc.*, (A), 641 (1967).
(5) C.A. McAuliffe, J.V. Quagliano, and L.M. Vallarino, *Inorg. Chem.*, *5*, 1996 (1966).

Table I. Analytical Data of the Complexes.

Complex	Colour	Melting point (decomp.) °C		C	H	N %	S	M
$Pd[SCH_2CH(NH_3^+)COO]_2$	Orange	184°	found:	20.6	3.4	7.8	18.4	30.5
			calculated:	20.8	3.5	8.0	18.5	30.7
$Pt[SCH_2CH(NH_3^+)COO]_2$	Yellow	182°	found:	16.5	2.6	6.0	14.6	44.4
			calculated:	16.6	2.8	6.4	14.7	44.6

Table II. Characteristic i.r. frequencies of the complexes.

*Ligand, L (cysteine) cm^{-1}	$Pd(L-H)_2$ cm^{-1}	$Pt(L-H)_2$ cm^{-1}	Assignment of bands
3012 (s, br)	3430 (s, br) 3088 (m, br)	3431 (s, br) 3082 (m, br)	NH_3^+ stretching
2568 (s)	absent	absent	SH stretching
1615 (vs)			NH_3^+ degenerate deformation
	1630 (s, br)	1630 (s)	
1590 (vs)			COO^- asymmetric stretching
1519 (vs)	1490 (m)	1490 (m)	NH_3^+ symmetric deformation
1400 (s)	1383 (s)	1382 (s)	COO^- symmetric stretching
945 (m)	absent	absent	SH bending
—	440 (s, br)	478 (m, br)	M-O stretching
—	378 (s)	375 (s)	M-S stretching

* ref.)1); vs - very strong, s - strong, m - medium. br - broad.

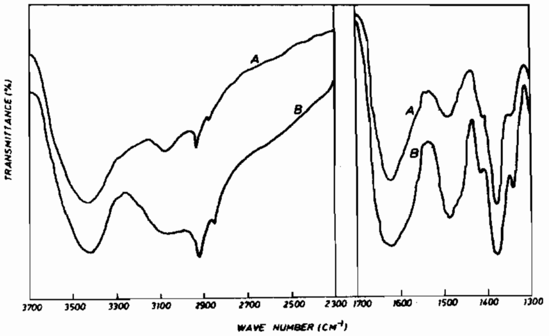


Figure 2. Infrared Spectra of (A) $Pt(L-H)_2$ and (B) $Pd(L-H)_2$.

Results and Discussion

Cysteine, having three coordination sites namely sulphhydryl, amino and carboxylate groups, can easily form 5-membered (N and S or N and O bonded) and 6-membered (S and O bonded) chelates with metal ions. Both $Pd(L-H)_2$ and $Pt(L-H)_2$ were found to be diamagnetic as expected for square planar Pd^{II} and Pt^{II} complexes. The electronic spectrum of $Pd(L-H)_2$ shows four absorption peaks. In square planar palladium complexes of N-N'-diphenylthiourea, $Pd^{II}[CS(NH\Phi)_2]_4Cl_2$, the absorption bands assigned[6] for d-d transition and S→Pd charge transfer are located at 23.5 kK and 33.6 kK respectively. In the case of $Pd(L-H)_2$, the maximum observed at 23.6 kK ($\varepsilon = 2.7 \times 10^3$) may be ascribed to d-d transition, characteristic of square planar Pd^{II} complex and the peak at 31.3 kK ($\varepsilon = 6.1 \times 10^3$) may be due to S→Pd charge transfer. The maxima at 37.0 kK and 47.6 kK are intraligand transitions that may be assigned to n-π* (>C=O:) and n-σ* ($-NH_2$) transitions[7].

The i.r. spectra of $Pd(L-H)_2$ and $Pt(L-H)_2$ (see Figure 2) are almost identical showing their similarity in structure and the type of bonding present. Compared with the spectrum of the free ligand,[1] cysteine, the following features are prominent.

(i) The strong intense absorption band observed for cysteine at 2568 cm^{-1} assigned to SH stretching and the medium intensity band at 945 cm^{-1} assigned to SH bending, are absent in the spectra of the complexes, indicating the deprotonation of the sulphhydryl group and coordination through the sulphur

(ii) The strong band at 1590 cm^{-1} in the ligand appears in the complexes at 1630 cm^{-1}. The broadness of the band may be due to the overlapping of ν_{asy} COO^- with the NH_3^+ degenerate deformation mode. In metal complexes of aminoacids wherein the COO^- is coordinated, the ν_{asy} COO^- is known to occur in the region 1580-1660 cm^{-1} [2,4]. The band at 1630 cm^{-1} therefore indicates that COO^- is also coordinating in the complexes. Further ν_{sym} COO^- in the ligand gets shifted to lower frequency in the complexes. This trend is in confirmity with the fact ν_{asy} COO^- in the free ligands, on coordination, shows a positive shift, whereas ν_{sym} COO^- shows a negative shift.

(iii) The NH frequency of a coordinated aminogroup generally appears in the region 3130-3280 cm^{-1}. The appearance of the NH band at the higher frequency (3430 cm^{-1}) is characteristic of a non-coordinated amino group. The medium intensity band observed at 1490 cm^{-1} in the complexes is assigned to NH_3^+ symmetric deformation mode.

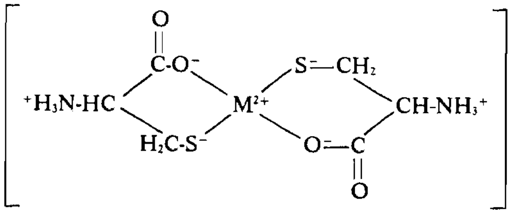
(6) T. Tarantelli and C. Furlani, *J. Chem. Soc. (A)*, 1717 (1968).

(7) C.N.R. Rao, « Ultra-violet and Visible Spectroscopy », Butterworth, London. (2nd edition), 1967 p. 15, 24.

Our arguments for the presence of coordinated -COO^- and non-coordinated -NH_3^+ groups are supported by similar previous assignments by McAuliffe[4] and Livingstone[2] in the complexes of methionine and S-methylcysteine with Pd^{II} and Pt^{II}.

IR spectral data in the range 200-650 cm^{-1} provided convincing proof for S- and O-coordination in the complexes Pd(L-H)_2 and Pt(L-H)_2. For several S-ligated Pd^{II} and Pt^{II} complexes, the metal-sulphur stretching vibrations are found to appear in the range 300-400 cm^{-1} [8-10]. Livingstone and Nolan assigned M-S stretching vibration in the range 378-385 cm^{-1} for the complexes ML'X_2 where M = Pd or Pt, L' = ethionine or S-methyl-L-cysteine and X = Cl or Br. Pd(L-H)_2 shows a band at 378 cm^{-1} and Pt(L-H)_2 at 375 cm^{-1} which are assigned to $\nu_{\text{Pd-S}}$ and $\nu_{\text{Pt-S}}$ vibrations respectively. Metal-oxygen stretching frequency for the oxalato complexes of Pd^{II} and Pt^{II} is reported to occur in the region 405-417 cm^{-1} and for palladium(II)acetylacetonate, it appears around 464 cm^{-1} [11]. The i.r. spectra of Pd(L-H)_2 and Pt(L-H)_2 show bands at 440 cm^{-1} and 478 cm^{-1} respectively which are assigned to $\nu_{\text{M-O}}$ vibrations. These bands are absent in the spectra of the free ligand. Also there is no band in the region 580-590 cm^{-1}, characteristic of Pd-N and Pt-N stretching,[12] indicating the absence of M-N bond in Pd(L-H)_2 and Pt(L-H)_2.

The insolubility of the complexes may suggest a polymeric structure by way of hydrogen bonding of the carboxyl group, as shown to be present in the complexes of methionine with PtCl_2 and PdCl_2[4]. But this possibility is ruled out in the complexes reported here because of the fact that the band around 1740 cm^{-1}, characteristic of an unionised -COOH group enabling hydrogen bonding, is absent in the spectra of the complexes. We, therefore, suggest the complexes reported here may have the following structure:



M = Pt or Pd

The possibility of isomerism exists in these complexes. Attempts are being made to isolate the isomers. Investigations are also in progress to isolate and characterise complexes of the type MLX, MLX_2, ML_2X_2 etc. (X = halogen) and to assess their reactivity patterns.

Both the complexes Pd(L-H)_2 and Pt(L-H)_2 are found to be insoluble in almost all common solvents like methanol, acetone, chloroform, carbontetrachloride, dimethylformamide and dioxan. Pd(L-H)_2, however, is very slightly soluble in water to the extent of 20 mg/1000 ml giving a pale yellow solution. The molar conductance of the aqueous solution is found to be 154 mhos cm^2 at 30°C, indicating uni-bivalent ions. This is probably due to the deprotonation of the NH_3^+ groups in the chelated complex in the solution phase to give $\text{H}_2[\text{Pd(L-2H)}_2]$. The low value of molar conductance, as compared to that expected for a typical 1:2 electrolyte, may probably be due to the less mobility of the bulky complex anion. The ionisation of the complex in aqueous medium is further supported by the ion-exchange studies: when the aqueous solution of the complex ($5.7\times10^{-5}\,M$) is passed through anionic resin column (in the Cl^- form), it is found that the complex gets adsorbed on the column. The eluate is colourless and is found to contain no palladium at all. When the aqueous solution of the complex is passed through cationic resin column (Na^+ form), the eluate is pale yellow in colour and is found to contain all the palladium originally taken. This shows that the complex has not been adsorbed on the cationic resin column. The above experiment, together with the conductivity studies, indicates that Pd(L-H)_2 on dissolution in water gives H^+ and $[\text{Pd(L-2H)}_2]^{2-}$ species.

The thermal behaviour of the complexes shows that the complexes begin to lose weight around 184° and the decomposition of the organic moiety is complete by 430°C. The final weight loss for Pd(L-H)_2 is found to be 64.6%, corresponding to the formation of PdO, which was confirmed by chemical analysis. The final weight loss for Pt(L-H)_2 is 55%, corresponding to the formation of platinum metal as the end product, also in confirmity with the chemical analysis.

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(10) J.R. Allkins and P.J. Hendra, *J. SChem. Soc.* (*A*), 1325 (1967).

(11) K. Nakamato, «)Infrared spectra of inorganic and coordination compounds », J. Wiley and Sons Inc., 1963, p. 217.

(12) G.W. Watt and D.S. Klett, *Inorg. Chem.*, 5, 1278 (1966).