

Some Thiosemicarbazide Complexes of Pt(II) & Pd(II)

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Ionic complexes of Pt(II) and Pd(II) with thiosemicarbazide (L) of the general formula ML_2X_2 where X = Cl, Br, I, CN, CNS, NO_3 or $\frac{1}{2}SO_4$ have been prepared from $H_2PtCl_6 \cdot xH_2O$ and $PdCl_2$ and using the method of substitution of the anion in ML_2Cl_2 . The preparation of two neutral complexes of the type $M(L-H)_2$ has also been described. Elemental analyses, magnetic and conductance measurements, UV and IR spectral data have been obtained. The complexes are probably square-planar. Existence of *cis-trans* isomerism among the complexes has been demonstrated.

METAL complexes with nitrogen and sulphur donors have been the subject of two recent reviews^{1,2}. In continuation of our earlier work on thiosemicarbazide (tsc) complexes of zinc group metals³, we are reporting here the results of our studies on complexes of Pt(II) and Pd(II) with tsc. Although the preparation of some of these complexes has been mentioned^{4,5} in literature, detailed studies have not been carried out.

Materials and Methods

Thiosemicarbazide (tsc) was a Merck reagent and it was recrystallized before use. $PdCl_2$ and $H_2PtCl_6 \cdot xH_2O$ (Johnson Matthey) were used as such. Magnetic measurements ($25^\circ \pm 2^\circ$) on the complexes were carried out using the Gouy method. X-ray powder patterns were obtained using Debye-Scherrer camera of diameter 114.6 mm with Co-K α ($\lambda=1.7902 \text{ \AA}$) radiation. Other experimental details have been reported elsewhere³.

Preparation of complexes: cis-PtL₂Cl₂—An ethanolic solution of $H_2PtCl_6 \cdot xH_2O$, was added dropwise to a hot solution of the ligand in minimum amount of ethanol in 1:2 ratio (metal-ligand). A buff-yellow complex separated from the solution after stirring. It was filtered, washed with hot ethanol and dried over P_2O_5 *in vacuo* (Found: C, 5.23; H, 2.10. Calc.: C, 5.35; H, 2.23%).

trans-PtL₂Cl₂ was prepared by mixing the reactants in ethanol in cold condition.

cis-PtL₂SO₄, *cis-PtL₂(NO₃)₂*, *trans-PtL₂Br₂*, *trans-PtL₂I₂*, *trans-PtL₂(CN)₂* and *trans-PtL₂(CNS)₂* were prepared by adding saturated aqueous solutions of the respective alkali sulphate (or 1:1 H_2SO_4), nitrate (or 1:1 HNO_3), halide, cyanide or thiocyanate to an ice-cold saturated aqueous solution of *cis-PtL₂Cl₂* in the stoichiometric ratio. The solids separated after stirring were filtered, washed with ice-cold water and recrystallized from aqueous solution.

cis-PtL₂SO₄ and *cis-PtL₂(NO₃)₂* can also be precipitated by adding 1:1 H_2SO_4 or 1:1 HNO_3 dropwise to a hot 1:2 aqueous mixture of $H_2PtCl_6 \cdot xH_2O$ and the ligand.

trans-bis(thiosemicarbazide) Pd(II) chloride—A solution of thiosemicarbazide (2 moles) in 2M HCl was added to a hot solution of $PdCl_2$ (1 mole) in 2M HCl with constant stirring. The complex which separated was filtered, washed with 0.1M HCl and dried over P_2O_5 *in vacuo* (Found: C, 6.72; H, 2.71. Calc.: C, 6.68; H, 2.78%).

The preparations of *trans-PdL₂SO₄*, *trans-PdL₂(NO₃)₂*, *trans-PdL₂Br₂*, *trans-PdL₂I₂*, *cis-PdL₂(CN)₂* and *cis-PdL₂(CNS)₂* were similar to those of the corresponding platinum complexes described above.

trans-PdL₂SO₄ and *trans-PdL₂(NO₃)₂* can also be precipitated respectively by adding tsc in 1:1 H_2SO_4 or 1:1 HNO_3 with constant stirring to a solution of $Pd(OH)_2$ dissolved in 1:1 H_2SO_4 or 1:1 HNO_3 , in 2:1 molar ratio. Corresponding *cis* complexes were obtained at higher temperatures.

trans-Pt(L-H)₂ and *trans-Pd(L-H)₂* were prepared respectively by the addition of excess 1M ammonia to aqueous solutions of the corresponding chloride complexes.

Results and Discussion

The analytical data (Table 1) of the complexes indicate the formation of two types of complexes; $M(L)_2X_2$ and $M(L-H)_2$ where M=Pd(II) or Pt(II), L=tsc and X=various anions.

The platinum complexes with the exception of PtL_2SO_4 and $Pt(L-H)_2$ are soluble in water, while the palladium complexes with the exception of PdL_2SO_4 , $PdL_2(CN)_2$ and $Pd(L-H)_2$ are moderately soluble in water. All the complexes are insoluble in common organic solvents.

Molar conductance measurements on $10^{-3}M$ aqueous solutions of the complexes at 25° show that the complexes are 1:2 electrolytes⁶ (Table 1). The electrolytic nature of the complexes was further verified by ion exchange experiments.

All the complexes are diamagnetic, as expected for square-planar complexes of Pt(II) and Pd(II).

UV and visible spectral data of the complexes have been obtained. The bands around 42 and 48 KK could be attributed to intra-ligand transitions, while those around 38 KK could be the charge-

TABLE 1 — PHYSICO-CHEMICAL DATA OF THE COMPLEXES

Complex	Found (Calc.), %				Decomp. temp. °C	ΔM (ohm ⁻¹ cm ⁻² mole ⁻¹)
	M	S	N	X		
<i>cis</i> -PtL ₂ Cl ₂ ^a	43.30 (43.50)	14.44 (14.31)	18.56 (18.74)	15.84 (15.83)	274	271
<i>trans</i> -PtL ₂ Cl ₂ ^b	43.60 (43.50)	14.40 (14.31)	18.97 (18.74)	15.74 (15.83)	271	269
<i>trans</i> -PtL ₂ Br ₂ ^a	36.86 (36.32)	12.09 (11.94)	16.10 (15.64)	29.45 (29.75)	294	268
<i>trans</i> -PtL ₂ I ₂ ^a	30.65 (30.91)	9.91 (10.16)	13.52 (13.31)	40.62 (40.21)	250	264
<i>trans</i> -PtL ₂ (CN) ₂ ^c	45.82 (45.43)	14.68 (14.93)	26.10 (26.09)	12.00 (12.12)	250	231
<i>trans</i> -PtL ₂ (CNS) ₂ ^d	40.00 (39.53)	26.23 (25.99)	22.80 (22.70)	23.14 (23.54)	185	196
<i>cis</i> -PtL ₂ (NO ₃) ₂ ^e	38.66 (38.91)	13.00 (12.79)	22.53 (22.35)	—	279	249
<i>cis</i> -PtL ₂ SO ₄ ^e	41.48 (41.21)	20.51 (20.32)	17.96 (17.75)	20.35 (20.28)	267	—
<i>trans</i> -Pt(L-H) ₂ ^f	51.23 (51.97)	16.92 (17.08)	22.20 (22.49)	—	235	—
<i>trans</i> -PdL ₂ Cl ₂ ^g	29.55 (29.83)	17.33 (17.80)	22.93 (23.36)	19.78 (19.74)	271	273
<i>trans</i> -PdL ₂ Br ₂ ^h	23.86 (23.72)	14.65 (14.30)	18.45 (18.74)	35.14 (35.63)	280	258
<i>trans</i> -PdL ₂ I ₂ ⁱ	19.50 (19.61)	11.90 (11.82)	15.47 (15.49)	47.11 (46.79)	235	243
<i>cis</i> -PdL ₂ (CN) ₂ ^h	30.93 (31.23)	18.92 (18.82)	33.00 (32.89)	—	209	—
<i>cis</i> -PdL ₂ (CNS) ₂ ^d	26.19 (26.28)	31.98 (31.68)	27.52 (27.68)	28.18 (28.69)	169	222
<i>cis</i> -PdL ₂ (NO ₃) ₂ ^g	25.96 (25.78)	15.25 (15.54)	26.50 (27.15)	—	272	239
<i>trans</i> -PdL ₂ (NO ₃) ₂ ^h	25.38 (25.78)	15.45 (15.54)	26.70 (27.15)	—	274	243
<i>cis</i> -PdL ₂ SO ₄ ⁱ	27.65 (27.62)	25.69 (25.00)	22.27 (21.84)	25.40 (24.97)	262	—
<i>trans</i> -PdL ₂ SO ₄ ^h	27.76 (27.62)	24.87 (25.00)	21.63 (21.84)	25.34 (24.97)	260	—
<i>trans</i> -Pd(L-H) ₂ ^d	36.94 (37.11)	22.65 (22.37)	29.19 (29.44)	—	201	—

a = buff, b = light buff, c = greenish white, d = greenish yellow, e = yellowish white, f = silky blue, g = light orange-yellow, h = orange-yellow, i = orange.

transfer bands of the groups S-Pt and S-Pd. The common bands around 28.5 and 23.5 KK may be ascribed to *d-d* transitions characteristic of square-planar complexes.

Tentative assignments of the IR bands in typical cases, based on previous work^{3,5,7}, are shown in Table 2.

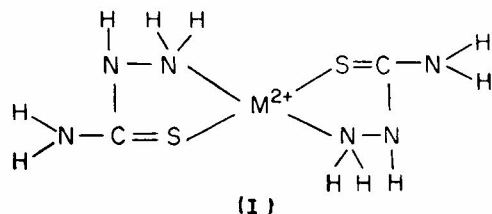
Upon complexation νNH modes of the ligand at 3389, 3285 and 3194 cm⁻¹ move to lower regions in the ionic complex while a shift towards higher wave numbers is noticed in the case of neutral species, M(L-H)₂. The formation of neutral complexes by dissociation of proton from the NH₂ group of the ligand may lead to strengthening of the remaining NH bond. The other site of co-ordination is thiocarbonyl sulphur atom as indicated by the downward shift of ν C=S by ~100 cm⁻¹ from the position observed in the ligand^{8,9}. Two strong bands at 1642 and 1623 cm⁻¹ (bending modes⁷ of NH₂ or combination of deformation mode of NH₂ and the amide-II band¹⁰) are not much affected by complex formation⁷. On the other hand, a strong band observed at 1531 cm⁻¹ in tsc, attributed to a coupled vibration of a NH rocking mode and CN stretch (β NH+νCN), is raised to higher frequencies in the ionic species, while it is unchanged in the neutral complexes. This increase is compatible with coordination through sulphur in which case the double bond character of the CN bond is expected to increase thereby affecting the contribution of νCN in the ionic complexes. Of the two moderately strong bands at 1487 and 1326 cm⁻¹ (νCN+αNH₂+νCS), the former moves to lower frequency region while the latter moves to higher frequency region¹⁰. The bands at 1290 cm⁻¹ (νCN+νCS) and 1172 and 1000 cm⁻¹ (αNH₂+βNH₂) are only slightly affected by complex formation. But a very important feature of the IR spectra of the neutral

TABLE 2 — INFRARED BAND POSITIONS (cm⁻¹) OF THIOSEMICARBAZIDE AND ITS COMPLEXES

tsc	<i>trans</i> -PdL ₂ Cl ₂	<i>cis</i> -PtL ₂ SO ₄	<i>trans</i> -Pd(L-H) ₂
3389S	3354S	3315VW	3456S
3285m	3248S	3208VW	3287m
3194m	3142W	3150VW	3215W(b)
1642S	1648S } ^d	1658VS	1640S } ^d
1623S	1621S } ^d	—	1600S } ^d
1531S	1580VW	1571VW	1531m
1487m	1450S	1467S	1458VW
1326m	1384m	1423m	1317VS
1290S	1342m	1383m	1231S
1172S	1239S	1275S	1147S
1000S	1158m	1098S(b)	1009VW
819S	1017VW	—	958VS
650S	700S	700S	700S
504S	621S(b)	614S	674m
—	498VW	511W	501S
—	431m	490VW	433VS
—	—	455W	—
—	—	440VW	—

complexes is the appearance of a strong band at 958 cm⁻¹. This is most likely the N-N stretch due to the elongation of N²-N³ bond and a charge localization on the C-N¹ bond^{3,5,11}. Bands around 650 cm⁻¹ and below in the ligand are assigned to skeletal vibrations¹².

Evidence for *cis-trans* isomerism among the complexes has been obtained from the IR data. Two sharp bands are shown by the *trans* isomer around 3400-3000 cm⁻¹ while the *cis*-isomer shows only a broad band. Also the *trans* isomer shows a doublet band around 1600 cm⁻¹ while a sharp single broad band is observed for the *cis*-isomer. Further, the *trans* compound is characterized by a single distinct peak at ~435 cm⁻¹ while a number of peaks are found in this region for the *cis* form.



X-ray powder patterns obtained broadly suggest a monoclinic crystal structure for the complexes and support the IR evidence. While the *trans* form shows only a few lines in its diffraction pattern, a large number of lines were obtained for the *cis* compound. The large number of bands and lines observed for the *cis* compounds could be attributed to the absence of centre of symmetry in these molecules.

It is to be noted that in the present studies, it was possible to obtain the *cis* form of PtL_2Cl_2 , while Haines and Sun⁵ were unsuccessful in their attempts to prepare this compound. Contrary to expectations, it was found that the *cis* form is stable for several months. In the method of preparation based on anion substitution, with *cis*- PtL_2Cl_2 , using Br^- , I^- , CN^- and CNS^- ions the *trans* form of the complexes was obtained. With NO_3^- and SO_4^{2-} ions, only the *cis* form was obtained. However, the neutral complexes were obtained in the *trans* form. Similarly with *trans*- PdL_2Cl_2 , *trans* forms of the complexes were obtained when Br^- , I^- , NO_3^- and SO_4^{2-} ions were used. The neutral complex was also obtained in the *trans* form. *cis* forms are obtained when CN^- and CNS^- ions are used. It is likely that there is a preference for the *trans* arrangement with some of these anions, which may be due to the interaction of the latter in the axial positions of the molecule.

From the physico-chemical data obtained for the complexes it may be safely assumed that the complexes are square-planar, with the metal ion coordinating through the sulphur and nitrogen atoms of the ligand. Structure (I) is proposed for the *trans* ionic complexes. Similar structures can be written for the *cis* form of the ionic complexes and *trans* form of the neutral complexes.

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