

PREPARATION AND ESTIMATION OF THIOSEMICARBAZIDE COMPLEXES OF PLATINUM AND PALLADIUM WITH CHLORAMINE-T AND DICHLORAMINE-T

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ABSTRACT

'Ionic' and 'neutral' complexes of thiosemicarbazide (TSC) with Pt and Pd, of the type $M(TSC)_2X_2$, and $M(TSC-H)_2$ respectively, (where $X = Cl, Br, I, CN, CNS$ and NO_3) have been prepared from $H_2PtCl_6 \cdot xH_2O$ and $PdCl_2$. The ligand in the complexes undergoes oxidation with chloramine-T and dichloramine-T, with a 24-electron change per molecule of the complex. Volumetric methods for the estimation of the complexes have been proposed.

THIOSEMICARBAZIDE (TSC) is well known as a metal complexing agent and also finds application in the characterization of aldehydes, ketones and polysaccharides. Since a number of metal complexes of the compound are known, suitable analytical techniques are essential for estimating the compound in the free state as well as in the complexes. The methods for its estimation reported so far, based on its oxidation by alkali metal hypohalites^{1,2} and lead tetra-acetate³, are limited to the estimation of small quantities and are slow. Chloramine-T (CAT) and recently dichloramine-T (DCT) have been successfully used in assaying TSC and some of its metal complexes⁴⁻⁶. In the present investigations, we have reported the preparation of some 'ionic' complexes of Pt(II) and Pd(II) and their volumetric estimation by CAT and DCT. The communication also reports the oxidation of two 'neutral' complexes of Pt and Pd by these oxidants.

EXPERIMENTAL

E-Merck thiosemicarbazide was purified by recrystallization from aqueous solution. $PdCl_2$ and $H_2PtCl_6 \cdot xH_2O$ (Johnson-Matthey Ltd., London) were used for preparing the complexes. Chloramine-T (Merck) was purified by the method of Morris *et al.*⁷ An approximately decinormal solution was prepared and standardized by iodometry. DCT was prepared by the method of Jacob and Nair⁸ and an approximately decinormal solution of the compound in glacial acetic acid was standardized by the iodometric method. UV spectra were obtained from Beckman DB spectrophotometer. IR spectra (KBr disc) were recorded on a Carl Zeiss UR-10 Infra red spectrophotometer.

Preparation of Complexes

$Pt(TSC)_2Cl_2$.—This was prepared by adding dropwise an ethanol solution of $H_2PtCl_6 \cdot xH_2O$ to a hot saturated solution of the ligand in ethanol, in slightly beyond 1:2 molar ratio. The buff colored complex separated was then filtered, washed with hot ethanol

and dried over P_2O_5 in vacuo. $Pt(TSC)_2Cl_2$ is readily soluble in water but is insoluble in alcohol.

$Pt(TSC)_2X_2$, where $X = Br, I, CN, CNS$ and NO_3 was prepared by adding saturated solutions of the respective alkali halide, cyanide, thiocyanate or nitrate to the ice cold aqueous solutions of $Pt(TSC)_2Cl_2$. The precipitate obtained after stirring was filtered and purified by recrystallization from aqueous solution.

$Pd(TSC)_2Cl_2$.—A solution of TSC in 2 M HCl was added to a 2 M HCl solution of $PdCl_2$ in 2:1 molar ratio, with constant stirring. The yellow precipitate of the complex was filtered, washed with 0.1 M HCl and dried over P_2O_5 in vacuo.

The preparation of $Pd(TSC)_2X_2$ where $X = Br, I, CNS$ and NO_3 was similar to the corresponding platinum complex described above.

The 'neutral' complexes $Pt(TSC-H)_2^*$ and $Pd(TSC-H)_2^*$ were precipitated as a silky blue solid and a greenish yellow solid respectively by the addition of 1 M ammonia to aqueous solutions of the corresponding chloride complex, until the solution becomes weakly alkaline.

The composition of the complexes was checked by elemental analyses. All the complexes were found to be diamagnetic, as expected for the square planar complexes. Conductivity measurements on aqueous solutions ($10^{-3}M$) of ionic complexes showed that they are 1:2 electrolytes.⁹ UV spectra of the complexes show an intra ligand band around $43,000\text{ cm}^{-1}$, while a charge transfer band (from sulphur to metal) is found around $37,000\text{ cm}^{-1}$. A common band at $28,510\text{ cm}^{-1}$ is attributed to a d-d transfer, characteristic of square planar complexes¹⁰.

Infrared spectra of the complexes showed that the N-H stretching frequencies around 3000 cm^{-1} in TSC are affected by complex formation¹¹. Further, the strong band at 800 cm^{-1} in TSC attributed to pure C-S stretch¹² shifts to lower regions by as much as 100 cm^{-1} in the complexes. It can safely be assumed that the co-ordination of the metal ion takes place through both the nitrogen atom of the hydrazine

* (TSC-H) represents $(H_2NNCSNH_2)$.

residue and sulphur atom of the ligand, as found in the case of zinc group complexes of TSC¹¹.

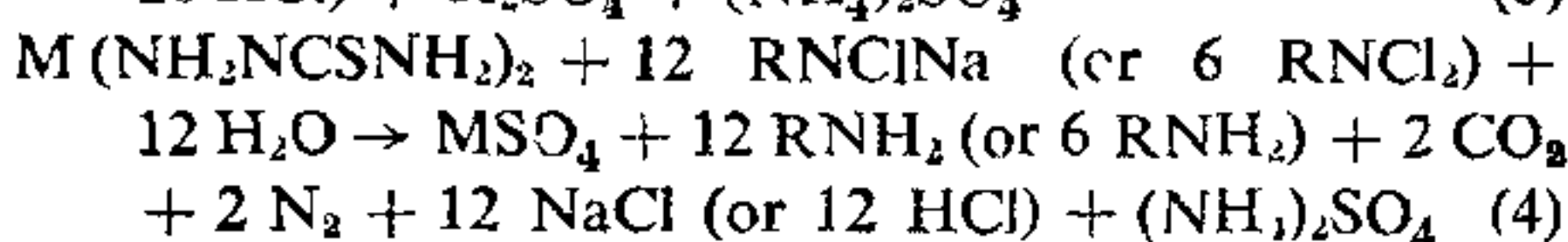
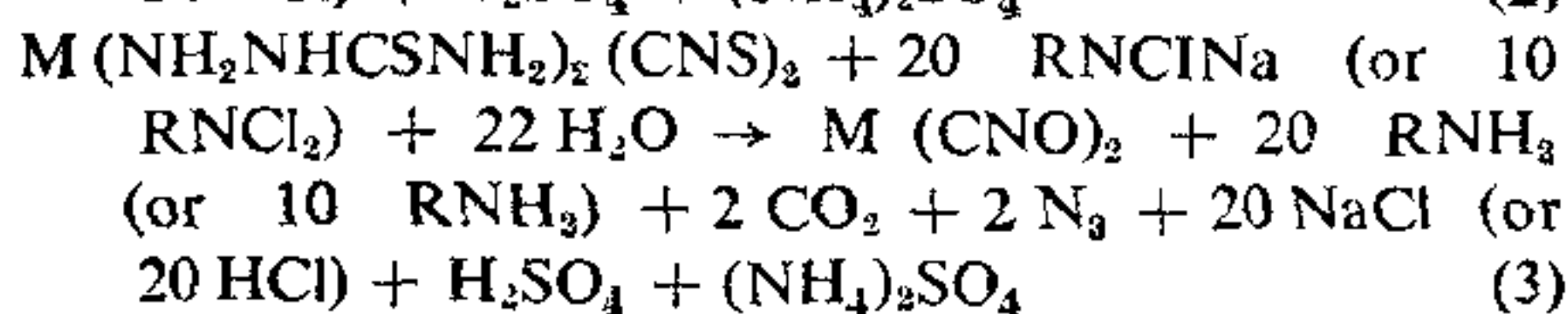
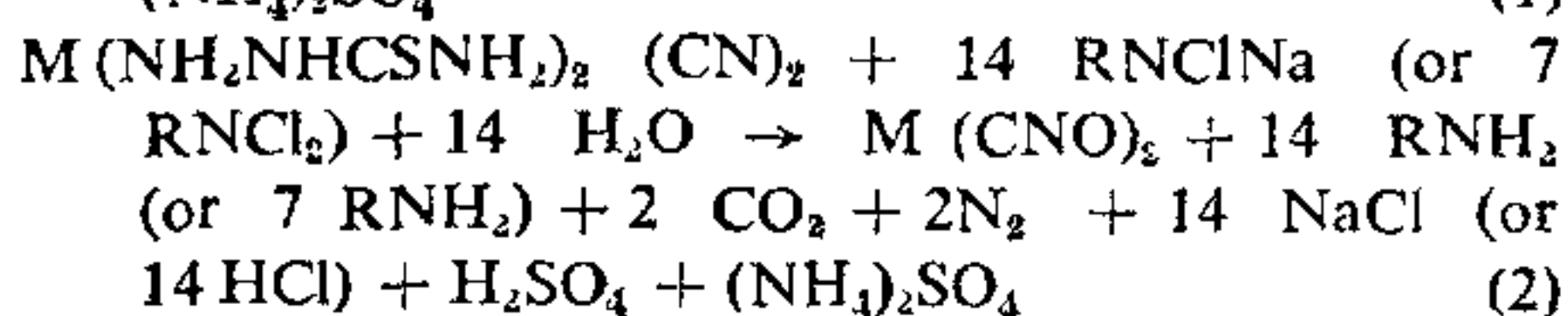
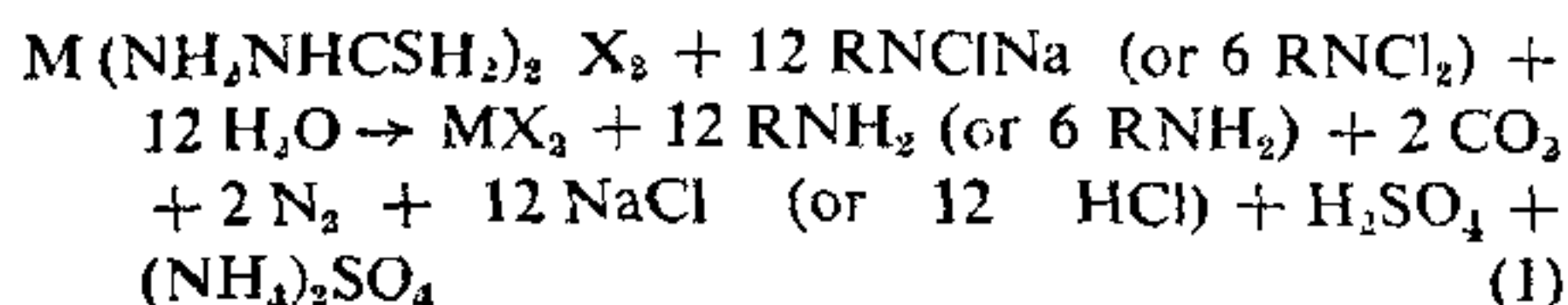
Some preliminary analytical investigations were carried out with the complexes. It was found that the ligand in the complexes was oxidized by CAT (with a 50–60% excess) at all pH. Oxidation was slow at pH < 1, faster in the pH range 1–3 and slower again at pH > 5. Oxidation was fastest at pH 4. Higuchi *et al.*¹³ have shown that monochloramine-T (RNHCl, where R = P-CH₃ - C₆H₄SO₂), formed in acidified solutions of CAT, disproportionates to DCT and *p*-toluene sulphonamide and the disproportionation rate is maximum around pH 4. The behaviour noticed with the oxidation of TSC complexes with CAT could probably reflect the high rate of disproportionation of the free acid RNHCl, which is also a fairly reactive species. Stoichiometric oxidation of the complexes took place within 30 minutes.

In oxidations with DCT, it was found that with a 50–60% excess of oxidant, the oxidation of the complexes (aqueous solutions or solutions in pH 4 buffer) was completed in 30 minutes, if an overall water content of about 10–15% was maintained in the reaction mixture. The rate of oxidation was found to be very slow with solutions of the complex in glacial acetic acid, the required stoichiometry being obtained after 16 hours⁶.

The ligand TSC in the complexes is oxidized by CAT or DCT with a 24 electron change per molecule of the complex. It was noticed that the anions CN⁻ and CNS⁻ present in the complexes are also oxidized by the oxidants under these conditions, with a 4-electron change¹⁴ and 16 electron change^{14,15} per molecule of complex respectively. Allowance was made for this fact in calculating the amount of complex recovered.

RESULTS AND DISCUSSION

The stoichiometry of oxidation of the complexes can be represented as follows:



Where M = Pt or Pd; X = Cl, Br, I or NO₃.

Recommended Procedure

Add aliquots of the complex (2–30 mg) solution in pH 4 buffer to 25 ml of 0.1 N CAT in an iodine flask. Shake the contents and set aside for about 30 minutes. Rinse down with about 20 ml of water, add 10 ml of 2N H₂SO₄ and 10 ml of 20% KI and titrate with 0.1 N sodium thiosulphate. Run a blank with CAT solution alone. A similar procedure is followed in oxidations with DCT⁶.

Some typical results of analyses are given in Table I. The values are accurate with an error around 0.5%.

It can be concluded from the investigations on metal complexes of TSC, that the number of ligand molecules present in a molecule of the complex, could easily be computed by oxidation with CAT or DCT.

TABLE I

Estimation of Platinum and Palladium complexes of thiosemicarbazide with chloramine-T and dichloramine-T

Complex	Range studied mg	% error in recovery		Complex	Range studied mg	% error in recovery	
		CAT	DCT			CAT	DCT
Pt (TSC) ₂ Cl ₂	2–30	0.2–0.5	0.0–0.5	Pd (TSC) ₂ Cl ₂	3–30	0.1–0.5	0.0–0.6
Pt (TSC) ₂ Br ₂	3–46	0.2–0.3	0.1–0.3	Pd (TSC) ₂ Br ₂	3–40	0.1–0.5	0.0–0.5
Pt (TSC) ₂ I ₂	3–47	0.1–0.5	0.3–0.4	Pd (TSC) ₂ I ₂	3–32	0.1–0.5	0.1–0.6
Pt (TSC) ₂ (CN) ₂	2–33	0.0–0.4	0.0–0.4	Pd (TSC) ₂ (CNS) ₂	2–30	0.3–0.5	0.0–0.5
Pt (TSC) ₂ (CNS) ₂	2–31	0.0–0.5	0.0–0.5	Pd (TSC) ₂ (NO ₃) ₂	2–30	0.2–0.5	0.1–0.4
Pt (TSC) ₂ (NO ₃) ₂	2–24	0.2–0.6	0.3–0.6	Pd (TSC-H) ₂	2–31	0.0–0.5	0.0–0.5
Pt (TSC-H) ₂	2–31	0.2–0.5	0.1–0.5				

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STUDY ON EQUILIBRIUM CONSTANTS OF UO_2^{2+} WITH MALONIC ACID AT DIFFERENT IONIC STRENGTHS

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ABSTRACT

The dissociation constants of the ligand and log K values of its complexes with uranyl ion have been investigated by Calvin-Bjerrum potentiometric titration technique at $30 \pm 0.1^\circ \text{C}$ and at various ionic strengths in aqueous medium. Uranyl forms both 1:1 and 1:2 complexes with malonic acid in the pH range 3–5. The plots of $\text{pK}/\log K$ vs. $\sqrt{\mu}$ were drawn to understand the exact complexation equilibria of 1:1 complex. The formation of 1:1 complex by the reaction $\text{UO}_2^{2+} + \text{HL}^- \rightleftharpoons \text{UO}_2\text{L} + \text{H}^+$ is confirmed. The thermodynamic constants at $\mu \rightarrow 0$ are reported.

INTRODUCTION

URANYL complexes of malonic acid were investigated by some workers^{1,2}. Ramamoorthy and Santappa³ have reported the uranyl complexes of malonic acid at 0.1 M NaClO_4 . The present paper reports the study of the stability constants of UO_2^{2+} malonic acid system in aqueous medium at various ionic strengths.

EXPERIMENTAL

The details regarding the chemicals, apparatus are given in our earlier paper⁴.

Calvin-Bjerrum Titration

The experimental procedure involved the potentiometric titration of carbonate free solution of (i) free HClO_4 ($4.40 \times 10^{-3} \text{M}$), (ii) free HClO_4 ($4.40 \times 10^{-3} \text{M}$) + malonic acid ($3.02 \times 10^{-3} \text{M}$), (iii) free HClO_4

($4.40 \times 10^{-3} \text{M}$) + malonic acid ($3.02 \times 10^{-3} \text{M}$) + uranyl ion ($4.32 \times 10^{-4} \text{M}$) against sodium hydroxide (0.18 N) added from a microburette.

The ionic strength of the solution was maintained by the addition of appropriate amount of 1 M sodium perchlorate solution. The exact ionic strength of the solution was calculated by taking $\mu = \frac{1}{2} \sum c_i z_i^2$ where c_i and z_i are the concentration and valency respectively of i -th ion,

RESULTS AND DISCUSSION

The probability of complex formation between UO_2^{2+} and the ligand anion was assumed and the factors like hydrolysis of uranyl ion and the formation of polynuclear species were neglected on the following points.

(i) The pH of hydrolysis of uranyl ion, obtained from the deviation of uranyl ion curve from the acid curve, was around pH 3.8. The departure of metal