

Photometric Titration of Se(IV) with Fe(II)*

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The pyridine (Py) complexes of $M(\text{SO}_3\text{Cl})_2$, where $M = \text{Co}$, Ni or Cu were prepared by treating the respective chlorosulphates with slight excess of pyridine in dry carbon tetrachloride and stirring the contents for 1 hr. The reaction took place in suspension and the resulting compounds were thoroughly washed with dry carbon tetrachloride followed by ether and finally dried *in vacuo*, to obtain respectively, a pink crystalline solid, $\text{Co}(\text{py})_4(\text{SO}_3\text{Cl})_2$ (Found: Co, 9.43; S, 10.29; Cl, 11.50; N, 9.13. Req'd: Co, 9.73; S, 10.56; Cl, 11.71; N, 9.24%), a light green crystalline solid, $\text{Ni}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ (Found: Ni, 10.13; S, 10.00; Cl, 11.65; N, 9.20. Req'd: Ni, 9.69; S, 10.57; Cl, 11.71; N, 9.24%) and a blue crystalline solid, $\text{Cu}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ (Found: Cu, 10.00; S, 10.28; Cl, 11.70; N, 9.21. Req'd: Cu, 10.40; S, 10.48; Cl, 11.63; N, 9.17%).

All the three complexes are hexa-coordinated having tetragonally distorted octahedral structures. The symmetry of the chlorosulphate group is lower than C_{3v} in all these complexes as the IR spectra show splitting of the doubly degenerate $\nu_4(\text{E})$ and $\nu_5(\text{E})$ modes. Three significant bands of pyridine, at 403 cm^{-1} (an out-of-plane ring deformation) and at 601 and 1578 cm^{-1} (in-plane ring deformation) shift to higher frequencies on coordination to metals¹. In all the three complexes these bands show an upward shift indicating that all the pyridine molecules are coordinated to the metal ions. Our results are in confirmity with those of Thompson and coworkers² who have reported similar observations for the compounds of the type $M(\text{Py})_4(\text{SO}_3\text{F})_2$ ($M = \text{Ni}$ and Co).

The electronic spectrum of $\text{Ni}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ exhibits bands at 16 and 25 kK assigned to ${}^3T_{1g}(\text{F}) \leftarrow {}^3A_{2g}(\text{F})$ and ${}^3T_{1g}(\text{P}) \leftarrow {}^3A_{2g}(\text{F})$ transitions. This indicates hexa-coordination of $\text{Ni}(\text{II})^3$. The bands at 19.2 and 21.5 kK in the electronic spectrum of $\text{Co}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ have been assigned to the transitions ${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g} \leftarrow {}^4T_{1g}(\text{F})$ consistent with those for octahedral $\text{Co}(\text{II})$ complexes⁴. The occurrence of a band at 14.3 kK in the electronic spectrum of $\text{Cu}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ attributable to ${}^2T_{2g} \leftarrow {}^2E_g$ transition, suggests that the complex has tetragonally distorted octahedral structure⁵.

The magnetic moments for $\text{Ni}(\text{Py})_4(\text{SO}_3\text{Cl})_2$, $\text{Cu}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ and $\text{Co}(\text{Py})_4(\text{SO}_3\text{Cl})_2$ are 3.14, 1.78 and 4.94 BM respectively. These values are in the range expected for hexa-coordinated complexes of these metals.

These hexa-coordinated complexes have the chlorosulphate groups coordinated as unidentate ligands. The behaviour of chlorosulphate groups in these complexes is analogous to that of other halogen or pseudohalogen groups.

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A direct photometric titration method has been developed for the determination of small amounts of selenium(IV). The method consists in titrating selenium(IV) with iron(II) in 80% phosphoric acid medium, in the presence of gum arabic, using blue-violet filter (maximum transmission 380-430 nm). About 150-800 μg of selenium can be determined with an accuracy of $\pm 0.9\%$. Chloride, sulphate, perchlorate and acetate ions do not interfere. A 10-fold excess of $\text{Te}(\text{IV})$ and a 100-fold excess of $\text{Te}(\text{VI})$ also do not interfere. Selenium(V₂) does not interfere up to a 10-fold excess. Copper(II) interferes.

TITRIMETRIC methods for the determination of selenium(IV) are mainly based on oxidation reduction reactions, most of them being indirect in nature¹⁻¹². These indirect methods utilize either excess of reductant or excess of oxidant and then back titrating the excess reagent. A few direct titrimetric methods are also known in which selenium(IV) is titrated with sodium hypochlorite or bromite¹³, mercury(I) nitrate¹⁴, chromium(II)¹⁵, titanium(III)¹⁶, potassium iodide¹⁷ or potassium permanganate¹⁸, the end-point being determined potentiometrically or photometrically. However, these direct methods, apart from requiring rigid conditions, suffer from the disadvantage that tellurium(IV) which is normally present along with selenium(IV) interferes. We have now developed a photometric titration of selenium(IV) with iron(II) in a strong phosphoric acid medium in which tellurium(IV) does not interfere.

Spectral studies were made using a Hilger Uvispek spectrophotometer using 1 cm glass cells. Photometric titrations were carried out using a Klett-Sumner photoelectric colorimeter with a No. 40 filter (maximum transmission 380-430 nm) and a rectangular $2 \times 4 \times 8$ cm glass cell (2 cm path length).

Selenium(IV) solution (0.05M) prepared from sodium selenite (BDH) was standardized by the method of Schrenk and Browning⁴. From this solution a 0.002M solution was prepared by suitable dilution.

An approximately 0.02M solution of iron(II) was prepared from ferrous ammonium sulphate (AR) and standardized with a standard solution of dichromate.

Syrupy phosphoric acid (Basynt, AR) of sp. gr. 1.75 (88%) was used. All other reagents used in this investigation were of AR grade.

Procedure—To an aliquot (1-5 ml) of selenium(IV) solution (containing ca 150-800 μg of selenium) taken in the glass cell, 36 ml of syrupy phosphoric acid and 3 ml of 20% solution of gum arabic were added and the volume made up to 45 ml. The

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TABLE 1 — PHOTOMETRIC DETERMINATION OF SELENIUM(IV) WITH IRON(II)

Amount of selenium (μg)		Error %
Taken	Found	
157.9	156.4	-0.9
236.9	238.4	+0.6
331.6	333.2	+0.5
394.8	391.6	-0.8
511.6	516.2	+0.9
631.7	635.9	+0.7
789.5	791.6	+0.3

solution was then titrated with iron(II). Stirring was provided by passing a stream of carbon dioxide. The passage of the gas was stopped before taking the absorbance readings. The titration was continued this way till the dial reading became constant. To get stable dial readings it required about 3 min in the beginning of the titration and about 9 min before the equivalence point. After the end-point was reached the absorbance values became constant within 1 min. Upon drawing a graph between the volume of the titrant and corrected absorbance two linear plots were obtained and the point of intersection of these lines corresponded to the end-point. Some representative results were presented in Table 1.

Selenium(IV), iron(III) and iron(II) have negligible absorbance in the region 350-750 nm in 80% (v/v) phosphoric acid medium. Elemental selenium in the presence of gum arabic is present in the form of an orange-red colloidal solution. The absorbance of this colloidal solution (in 80% phosphoric acid medium in the presence of 1% gum arabic) is maximum at 350 nm and gradually decreases with increase in wavelength. Since a filter corresponding to a wavelength of 350 nm was not available, the titration was monitored using a blue-violet filter (380-430 nm).

Beer's law was found to be obeyed up to a concentration of 15.79 $\mu\text{g}/\text{ml}$ using a cell of 2 cm path length. The accuracy of the method is $\pm 0.9\%$. The precision of the method was determined by titrating ten samples, each containing 473.7 μg of selenium, a value approximately in the middle of the optimum range. The mean value was found to be 472.4 μg with a standard deviation of 3 μg .

Chloride, sulphate, perchlorate and acetate ions do not interfere. A 10-fold excess of Te(IV) and a 100-fold excess of Te(VI) do not interfere. Selenium(VI) does not interfere up to a 10-fold excess; above this concentration it interferes by slowly getting reduced to elemental selenium. Copper(II) interferes.

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Complexes of Salicylidene-*o*-aminothiophenol with Pd(II), Hg(I & II) & Ag(I) & Its Use as a New Analytical Reagent for Their Amperometric Determination

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Salicylidene-*o*-aminothiophenol, the Schiff base derived from *o*-aminothiophenol and salicylaldehyde, has been used for the amperometric determination of Pd(II) (at an applied voltage of -0.44 V vs SCE), Hg(I and II) and Ag(I) (at -0.55 V vs SCE) using dropping mercury electrode as the indicator electrode. 12-21.3 ppm of Pd(II), 60-100 ppm of Hg(II), 120-200 ppm of Hg(I) and 50-108 ppm of Ag(I) can be determined with an accuracy of $\pm 0.5\%$. A number of foreign ions including Pt(IV), Ir(III), Au(III) and Bi(III) do not interfere even if present in 5-10 fold excess while traces of Ru(III) and Rh(III) interfere. The solid metal complexes have also been isolated and characterized.

WE report here the amperometric determination of Pd(II), Hg(II), Hg(I) and Ag(I) using salicylidene-*o*-aminothiophenol as a new analytical reagent. Structures of the solid complexes formed have also been investigated using analytical, conductance and IR data.

All physical measurements were carried out as reported¹ previously. The stock solutions of palladium chloride and mercurous nitrate were prepared in 0.2M hydrochloric acid and dilute nitric acid respectively while those of others were prepared in doubly distilled water. All the reagents were of AR (BDH) quality. The ligand (m.p. $136^\circ \pm 1^\circ$) was synthesized by the condensation of salicylaldehyde and *o*-aminothiophenol as described earlier².

The pK_1 and pK_2 values of the ligand as determined by potentiometric half-titration method³ were 7.1 and 9.8 respectively. Pd(II) was found to form 1:1 and 1:2 metal-ligand complex in the concentration ranges 0.0005/0.0002M and 0.1-0.0005M