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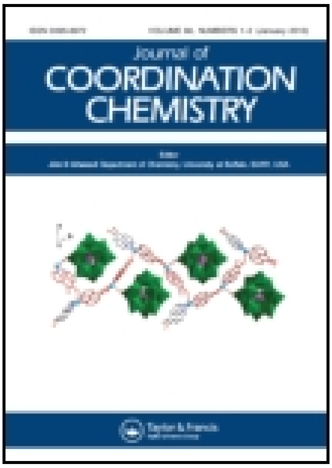

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Complexation of palladium(II) with thiocyanate - a spectrophotometric investigation

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Complexation of palladium(II) with thiocyanate – a spectrophotometric investigation

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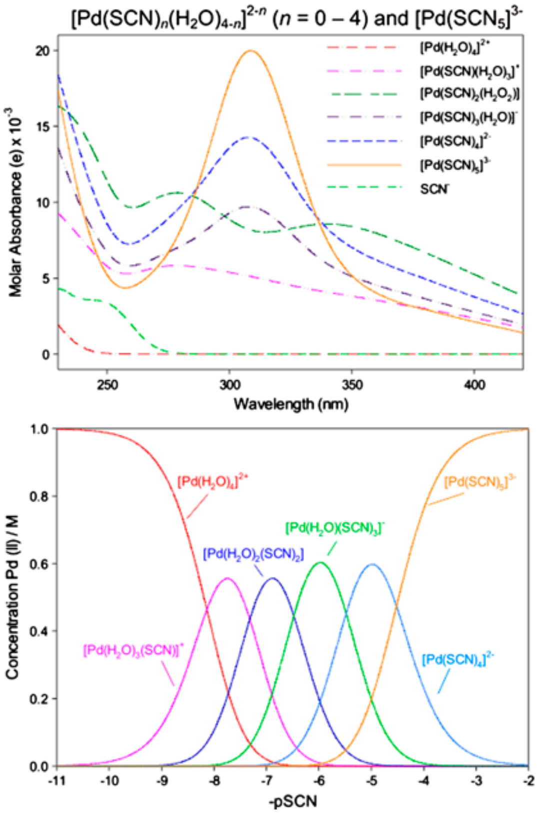

A spectrophotometric investigation into the complexation of palladium(II) with thiocyanate revealed the existence of five coordinated palladium(II) complexes. Molar absorbance spectra as well as formation constants were calculated for all five complexes.

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Complex-formation of Pd(II) with thiocyanate has been investigated by spectrophotometry at 25 °C and an ionic strength of 1.0 M. The formation constants, β_n, for the palladium(II) thiocyanate complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0–4$), have been determined and the values are: $\log\beta_1 = 8.14$, $\log\beta_2 = 15.46$, $\log\beta_3 = 21.94$, and $\log\beta_4 = 27.42$. These complexes are generally accepted to be square planar. However, a five-coordinate species, i.e. $[Pd(SCN_5]^{3-}$, with a formation constant of $\log\beta_5 = 31.94$ seems to exist and is proposed to be square pyramidal. Molar absorption spectra for all the complexes in question have been obtained.

Keywords: Palladium(II); Thiocyanate; Complexation; Formation constants; Spectrophotometry

1. Introduction

Hydrometallurgical processes play an important role in the processing, refining, and recycling of the platinum group metals and are typically divided into three general areas, leaching, solution purification, and metal recovery. Subsequent to leaching, the leach liquor has to undergo concentration of the metal ions that are to be recovered. As some undesirable metals may have also been taken into solution during the leaching process, the solution is often purified to eliminate these undesirable components. The two most common purification techniques employed are solvent extraction and ion exchange. With solvent extraction, a mixture of an extractant in a diluent is used to extract a metal from one phase to another and with ion exchange chelating agents, natural zeolite, activated carbon, resins, and liquid organics impregnated with chelating agents are all employed to exchange cations or anions within the solution [1–4]. A crucial foundation for all of the above-mentioned processes towards the development of any hydrometallurgical process is speciation, i.e. knowledge of the identity and distribution of specific metallic species in the solution. This would involve, in part, the construction of E_h–pH diagrams by which the stability regions of different metal complexes can be determined. To that regard, information on the formation constants of both noble metals and base metals is imperative for the development of effective separation processes. Information on the formation constants of the platinum group metal complexes in solution is not readily available. The United States' National Institute of Standards and Technology database of critically selected stability constants for metal complexes, as well as the IUPAC stability constants database, lists extremely limited data with regard to PGM complexes [5–7].

The palladium thiocyanate system is one such system for which the stability constants are extremely limited. Only a few papers are available and they only report values for $\log\beta_2$ and $\log\beta_4$. Apart from the data being limited, these values differ considerably. For $\log\beta_{2,}$ only one reported value of 16.20 [8] is available, whereas reported values for $\log\beta_4$ are 19.46 [9], 25.6 [8], 27.20 [10], 27.60 [11], 28.22 [12], and 28.67 [13].

The determination of $\log\beta_2$ by Joshi *et al.* [8] entailed the preparation of a solution of palladium(II) with a known quantity of chloride as a starting material. The complexation of Pd(II) with SCN^- was expressed as mixed complexes (equation (1)).

$$PdCl_m + nSCN^- \rightleftharpoons Pd(SCN)_nCl_{m-n} + nCl^- \tag{1}$$

The nature of the complexes was determined employing both Job's continuous variation method and the slope ratio method using different individual solutions that contained specific ratios of Pd(II) and SCN^- with an excess of Cl^-. For the latter method, palladium chloride was used as a source of palladium and the chloride concentration was kept constant while the solution was titrated with thiocyanate. These methods enabled the authors to spectrophotometrically calculate both $\log\beta_2$ and $\log\beta_4$ for the complexation of palladium with thiocyanate [8].

Other experimental methods employed mainly consisted of competition reactions between ligands having known stability constants with Pd(II) and thiocyanate [11–13]. This method limited the authors to calculate only one of the $\log\beta$ values due to the nature of the technique. The most recent literature on the complexation of palladium thiocyanate communicated a $\log\beta_4$ value of 27.20 [10]. The authors employed a rather complex competition reaction method where a solution of $[\mathrm{Pd(SCN)_4}]^{2-}$ and 2,2,2-tet was prepared at pH 2 and then titrated with a base until a transition pH was reached. The 2,2,2-tet complex was deprotonated and the red $[\mathrm{Pd(SCN)_4}]^{2-}$ ion was broken down to give the colorless [Pd (2,2,2-tet)]$^{2+}$ complex, which was used to calculate $\log\beta_4$ for the $[\mathrm{Pd(SCN)_4}]^{2-}$ complex (equations (2) and (3)).

$$[\mathrm{Pd(SCN)_4}]^{2-} + 2,2,2\text{-tet} + \mathrm{H}^+ \rightleftharpoons [\mathrm{Pd(2,2,2\text{-}tetH)SCN}]^{2+} + 3\mathrm{SCN}^- \quad (2)$$

$$[\mathrm{Pd(2,2,2\text{-}tetH)SCN}]^{2+} \rightleftharpoons [\mathrm{Pd(SCN)_4}]^{2+} + \mathrm{SCN}^- + \mathrm{H}^+ \quad (3)$$

As yet no values for $\log\beta_1$ and $\log\beta_3$ have been reported.

In this study, the aim was to use the palladium tetra–aqua complex $[\mathrm{Pd(H_2O)_4}]^{2+}$ as the starting material and titrate it with different volumes of a specifically prepared NaSCN solution to calculate the formation constants for the $[\mathrm{Pd(SCN)}_n\mathrm{(H_2O)}_{4-n}]^{2-n}$ ($n = 0$–4) system. The expected reaction scheme is shown below (equation (4)).

$$[\mathrm{Pd(H_2O)_4}]^{2+} + n\mathrm{SCN}^- \rightleftharpoons [\mathrm{Pd(SCN)}_n\mathrm{(H_2O)}_{4-n}]^{2-n} \quad (n = 0 - 4) \quad (4)$$

The same procedure was employed as in our earlier determination of the formation constants for $[\mathrm{PdCl}_n\mathrm{(H_2O)}_{4-n}]^{2-n}$ ($n = 0$–4) and $[\mathrm{PdCl}_p\mathrm{(OH)}_q]^{2-}$ ($p = 3$–0 and $q = 1$–4) [14].

2. Experimental

All reagents (Sigma Aldrich) were of analytical grade and solutions were prepared with water obtained from a Millipore Milli-Q system. Perchloric acid was standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide.

Palladium sponge was dissolved in a mixture of concentrated perchloric acid ($\mathrm{HClO_4}$) and fuming nitric acid ($\mathrm{HNO_3}$). The nitric acid was driven-off by careful heating and the procedure was repeated until all the palladium was dissolved with the palladium subsequently being oxidized to palladium(II). A stock solution of palladium(II) with a concentration of 3×10^{-3} M (confirmed by ICP analyses) and 1.0 M with regard to perchloric acid was prepared. From this solution, an 8.0×10^{-5} M palladium solution was prepared which was 0.974 M with regard to $\mathrm{NaClO_4}$ and 0.026 M with regard to $\mathrm{HClO_4}$. A sodium thiocyanate (NaSCN) stock solution of 5.0×10^{-4} M was prepared that was also 0.974 M with regard to $\mathrm{NaClO_4}$ and 0.026 M with regard to $\mathrm{HClO_4}$, thereby ensuring constant pH and constant ionic strength (1.0 M) within the reaction vessel when palladium(II) and thiocyanate were titrated employing these two solutions.

Initial efforts to conduct the titration in a reaction vessel coupled to a 'sipper system,' which pumped the solution by means of a small peristaltic pump through a flow-through cuvette, failed due to the fact that early precipitation was initiated as a result of stirring and pumping. As a result of this, due to the low solubility of $[Pd(SCN)_2(H_2O)_2]$ (log $K_{sp} = -17.8$ [16]), a batch titration method was subsequently employed. A Metrohm 809.1 double burette auto-titrator was used to prepare 69 individual solutions containing 20 mL 8.0×10^{-5} M palladium solution and different volumes of the thiocyanate solution. This resulted in the thiocyanate concentration varying from 4.95×10^{-6} to 2.80×10^{-4} M and the palladium concentration varying from 7.92×10^{-5} to 3.52×10^{-5} M as a result of dilution. This small change in the concentration was accounted for when the different models were built and the formation constants were calculated using HypSpec [15]. Absorption spectra were recorded immediately thereafter within the wavelength range of 200–500 nm against water as reference at 25 °C. An Analytic Jena SPECORD® S600 UV–vis diode-array spectrophotometer, equipped with a quartz cuvette with a path length of 10 mm, was used for the absorption measurements. Equilibrium was reached instantaneously as no further change in the spectra of the solutions were observed over time and the precipitation of $[Pd(SCN)_2(H_2O)_2]$ only occurred after a few minutes. The end result of this method is the same as a normal titration and to that regard the absorption data, within HypSpec, is handled the same way as with a normal titration.

Three initial titrations, with larger concentration change increments, were carried out to determine the concentration range and repeatability. This information was then used to subsequently conduct further two titrations having smaller changes in the consecutive thiocyanate concentrations. A slight difference in the sigma value for the last two titrations was observed (8.94×10^{-3} and 8.23×10^{-3}, respectively) and the best-fitted data (lowest Sigma value) was used for the determination of the different stability constants with the standard deviations (from the HypSpec analysis) only calculated for the final titration data-set.

Competition of H^+ for SCN^- and the subsequent formation of HSCN are negligible in that the pK_a of HSCN is –1.85 [16]. A high free thiocyanate concentration at the desired perchlorate concentration is therefore ensured.

3. Results and discussion

The two main difficulties that had to be overcome employing this approach were (i) the low solubility of $[Pd(SCN)_2(H_2O)_2]$ and (ii) obtaining reasonable absorbances to calculate the corresponding $\log \beta$ values. To prevent the influence of precipitation having an effect on the calculation of the model, individual samples were prepared simulating a titration (as explained above). The palladium concentration was kept below 8.0×10^{-5} M and the possibility of the formation of polynuclear palladium species is highly unlikely. Polynuclear species exhibit weak d-d bands in the UV–near–visible spectral region [17] and the fact that no change in the absorption spectra was observed within this region confirms that no polynuclear species were formed. The change in absorption spectra with increasing thiocyanate concentration is shown in figure 1. A number of observable changes in the absorption spectra together with the absence of an isosbestic point allude to the existence of three or more species.

Similar to Harrington *et al.* [10] reporting that the four-coordinated $[Pd(SCN)_4]^{2-}$ exhibits a maximum absorption at 308 nm, we observed a major peak at 309 nm and therefore

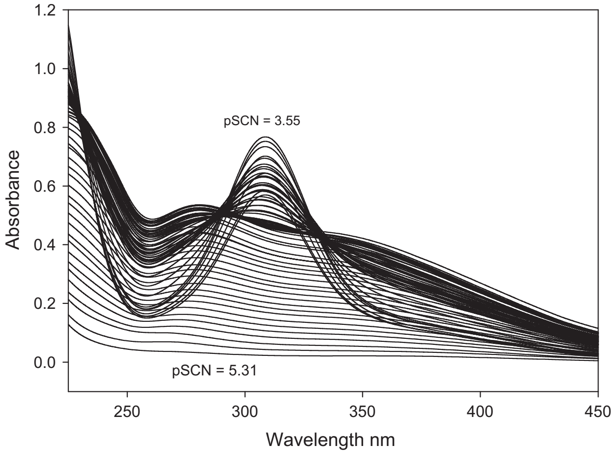

Figure 1. Change in absorption spectra with change in thiocyanate concentration.

focused our attention around this region. No recorded UV spectra or any molar absorbance spectra have been reported for the palladium thiocyanate system. Absorption data at every wavelength (every 0.5 nm) in the range 230–450 nm were treated with the program HypSpec 2009 to calculate equilibrium constants and absorption spectra for the initial complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4). The molar absorption spectra for thiocyanate as well as for the aqua complex $[Pd(H_2O)_4]^{2+}$ were calculated independently under the same conditions (ionic strength and temperature) and were supplied as known spectra to HypSpec.

A measure of the overall quality of data refinement is indicated by the sigma (σ) value, derived from the squared residual r (equation (5)), where m is the number of data points, n the number of parameters, and w the weight as part of a least-squared calculation. The weighting scheme accounts for error in absorbance measurements and is specific to each spectrophotometer.

$$\sigma = \sqrt{\frac{\sum_i w_i r_i^2}{m - n}} \tag{5}$$

With a correct weighting scheme, the value of the scaled sum of squares (σ) has an expected value of unity. An absolute weighting scheme with a linear weighting function (chosen within HypSpec) was employed as part of this study, which is appropriate for the Analytic Jena SPECORD® S600 UV–vis diode-array spectrophotometer. A refinement is good if the calculated values agree with the observations within the limits of experimental error. Subsequent to the repeated experimentation, it was found that the model that fitted the data the best, judged by the lowest sigma value, includes the five coordinate $[Pd(SCN)_5]^{3-}$. Good correlation between the actual and calculated titration curves at 240, 260, 280, and 309 nm, where major changes in the spectra are observed, highlights the legitimacy of this five-coordinate model (figure 2). Formation constants for models consisting of any number of complexes less than five could not be obtained as these models did not refine.

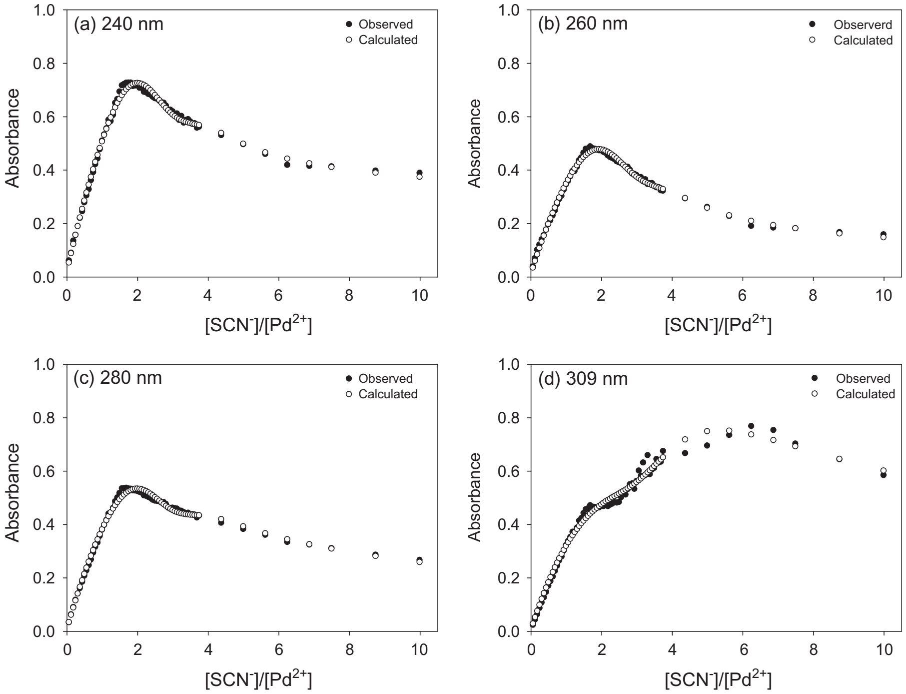

Figure 2. Actual/observed *vs.* calculated titration curves at specific wavelengths.

The values of the cumulative formation constants for the complexes $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[Pd(SCN)_5]^{3-}$ are $\log \beta_1 = 8.14$, $\log \beta_2 = 15.46$, $\log \beta_3 = 21.94$, $\log \beta_4 = 27.42$, and $\log \beta_5 = 31.94$. The $\log \beta_2$ and $\log \beta_4$ values, calculated by us as part of the overall model, correspond well with those values obtained from the literature and are therefore a very good indication of the reliability of the other overall model and formation constants, i.e. for $[PdSCN(H_2O)_3]^+$, $[Pd(SCN)_3H_2O]^-$, and $[Pd(SCN)_5]^{3-}$, and for the existence of these complexes under the experimental conditions, which is now reported for the first time. A summary of the different formation constants is presented in table 1 together with the corresponding literature values. It is clear that a fair correlation exists between our value for $\log \beta_2$ (15.55) and the only published value of 16.20 [8]. Furthermore, of the six values reported for $\log \beta_4$, our value of 27.42 correlates well with two values reported, i.e. 27.20 [10] and 27.60 [11]. This provides further confirmation to the legitimacy of our model.

Table 1. Formation constants for $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 1$–4) and $[Pd(SCN)_5]^{3-}$ at 1.0 M ionic strength and 25 °C (N/A = not available, $\sigma = 8.23 \times 10^{-3}$).

n	Complex	Literature	$\log \beta_n$
1	$[PdSCN(H_2O)_3]^+$	N/A	8.14 ± 0.026
2	$[Pd(SCN)_2(H_2O)_2]$	16.20 [8]	15.46 ± 0.024
3	$[Pd(SCN)_3(H_2O)]^-$	N/A	21.94 ± 0.096
4	$[Pd(SCN)_4]^{2-}$	19.46 [9], 25.60 [8], 27.20 [10] 27.60 [11], 28.22 [12], 28.67 [13]	27.42 ± 0.274
5	$[Pd(SCN)_5]^{3-}$	N/A	31.94 ± 0.277

From the equilibrium constants, a distribution curve was constructed showing the complete speciation of the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system and $[Pd(SCN)_5]^{3-}$ employing a total Pd concentration of 1 M as an example (figure 3). At the maximum thiocyanate concentration for this investigation, i.e. at 2.80×10^{-4} M and at a palladium concentration of 3.52×10^{-5} M, more than 90% of the palladium is in the form of the pentathiocyanate complex $[Pd(SCN)_5]^{3-}$.

In most cases palladium(II) complexes are square planar [18–20], but some authors have suggested the possibility of palladium forming a five-coordinate trigonal–bipyramidal complex [21]. Desmarais *et al.* [22] have obtained a new class of palladium(II) olefin complex, which is five coordinate, using a specific nitrogen bidentate ligand. Similar work has been conducted by Albano *et al.* [23] who produced five-coordinate olefin complexes of palladium(II). In addition, Lopez-Torres *et al.* [24] investigated the reaction of cyclometalated halide-bridged palladium(II) complexes with a tertiary triphosphine ligand to produce a complex with a five-coordinate palladium as confirmed by spectroscopic and analytic data. We modeled the five-coordinate $[Pd(SCN)_5]^{3-}$ complex, employing Accelrys Materials Studio 5.5, starting out with the trigonal–bipyramidal structure and allowing it to stabilize. The structure changed from the trigonal–bipyramidal structure to a square pyramidal configuration (figure 4) in both cases where the ligand binds to the metal through either nitrogen or sulfur. This was confirmed by modeling in Avogadro [25, 26] in that the trigonal–bipyramidal structure also stabilized in the square pyramidal configuration (figure 5).

The molar absorption spectra for all complexes are shown in figure 6. $[Pd(SCN)_5]^{3-}$ has the strongest charge transfer band at 309 nm. In the case of the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ system the charge transfer bands shifted to shorter wavelengths (higher energies) when chloride was substituted by water [14]. It is therefore expected that the charge transfer bands in the case of the $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system, as well as for $[Pd(SCN)_5]^{3-}$, will also shift towards shorter wavelengths with substitution of thiocyanate by water; in the present

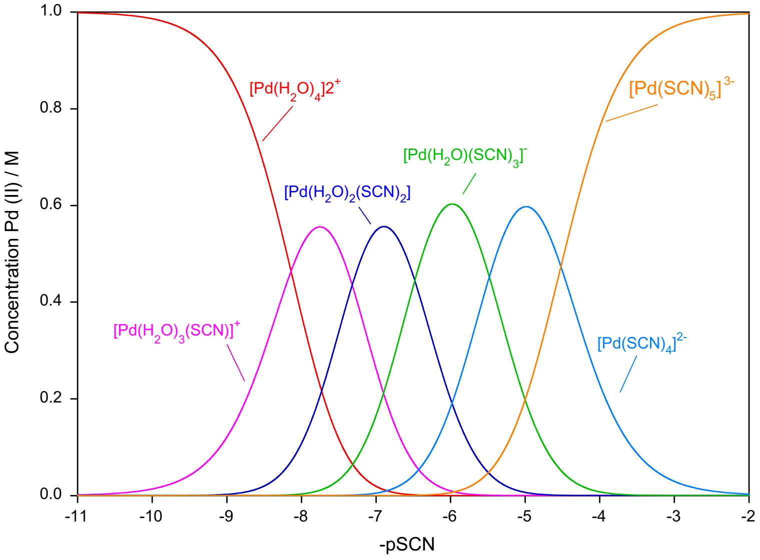

Figure 3. Distribution of $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[Pd(SCN)_5]^{3-}$ species as a function of –pSCN.

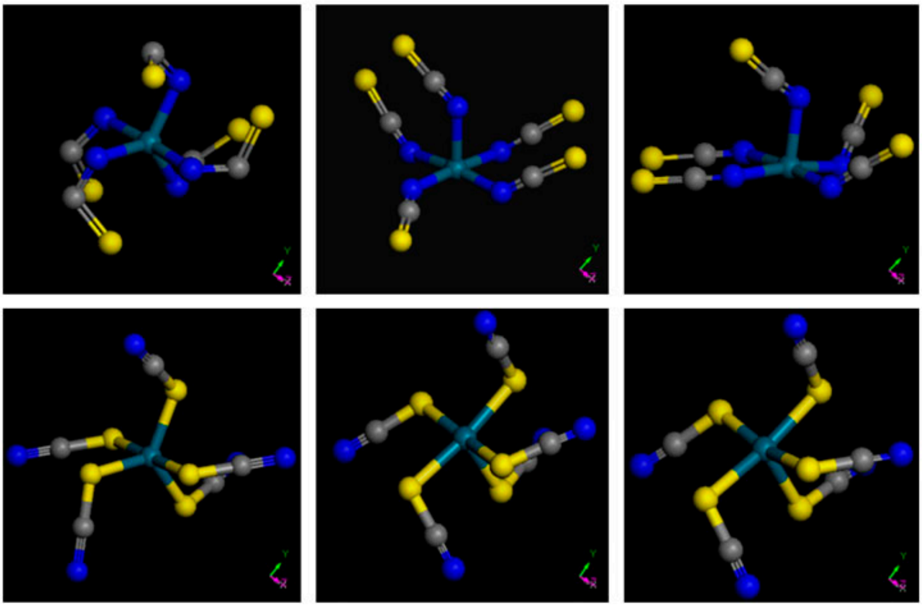

Figure 4. Modeled configurations of the five-coordinate $[Pd(SCN)_5]^{3-}$ complex showing the change from trigonal-bipyramidal (at the left) to square pyramidal (to the right).

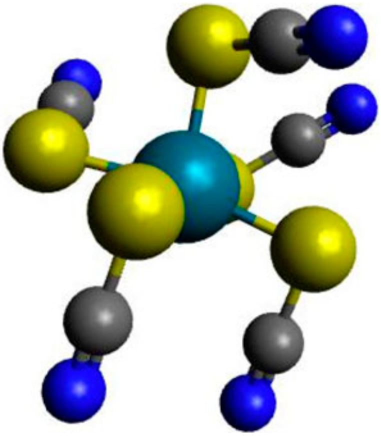

Figure 5. The stabilized five-coordinate $[Pd(SCN)_5]^{3-}$ complex as modeled by Avogadro [25, 26].

case even more so. Due to the pi-bonds present within the thiocyanate ligand, one would expect it to be the main chromophore in the different complexes. This also explains why there is a similarity between the absorbance spectra of some of the complexes. The highest absorbance is for the most substituted complex, $[Pd(SCN)_5]^{3-}$ (figure 6), which fits well with the statement of SCN^- being the main chromophore.

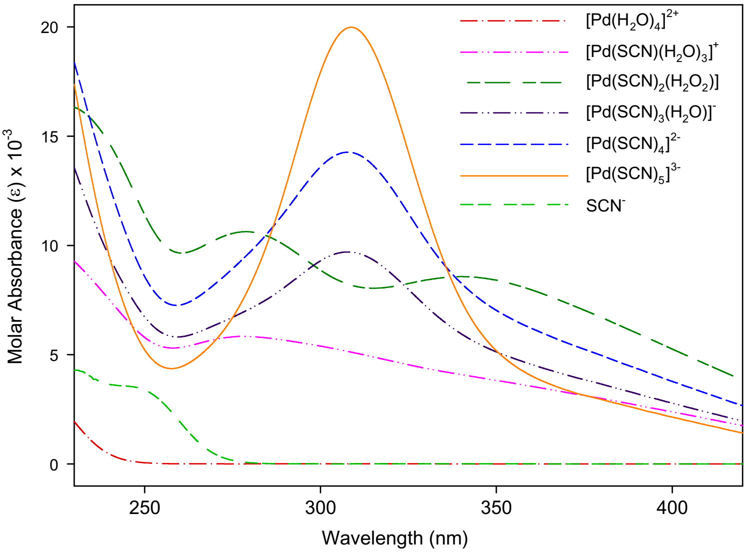

Figure 6. Calculated molar absorption spectra of $[Pd(SCN)_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) and $[Pd(SCN)_5]^{3-}$.

4. Conclusion

A successful spectrophotometric investigation into the complexation of palladium(II) with thiocyanate, i.e. obtaining a relevant and true sequential series of absorption spectra, modeling and proper data fitting, depended on preventing the precipitation of $[Pd(H_2O)(SCN)_2]$. This could not be accomplished by automated titration into a reaction vessel followed by circulation of the solution by means of a peristaltic pump through a flow-through cuvette as it was ascertained that mechanical stirring and pumping accelerated precipitation. This could be circumvented by making up individual solutions, also employing automated titration, and capturing the absorption spectrum immediately after proper mixing for each solution. The only model that fit the data involves the formation of five sequential complexes. Values for the formation constants of the five palladium(II) thiocyanate complexes, i.e. $[Pd(SCN)(H_2O)_3]^{+}$, $[Pd(SCN)_2(H_2O)_2]$, $[Pd(SCN)_3(H_2O)]^{-}$, $[Pd(SCN)_4]^{2-}$, and $[Pd(SCN)_5]^{3-}$, have been determined at an ionic strength of 1.0 M and a temperature of 25 °C. The formation constants are $\log\beta_1 = 8.14$, $\log\beta_2 = 15.46$, $\log\beta_3 = 21.94$, $\log\beta_4 = 27.42$, and $\log\beta_5 = 31.94$, with formation constants for the one-, three-, and five-coordinated complexes being reported here for the first time. Within this five-coordinate model, our values of $\log\beta_2$ (15.46) and $\log\beta_4$ (27.42) are in good agreement with the reported values, i.e. 16.20 [8] for the two-coordinate complex and 27.20 [10] and 27.60 [11] for the four-coordinate complex. This supports the legitimacy of this five-coordinate model. Molecular modeling furthermore postulates that the five-coordinate $[Pd(SCN)_5]^{3-}$ complex is square pyramidal.

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