Canadian Journal of Chemistry

Research Article

Identification of ruthenium chloride complexes in the coordination precursor *Ruthenium Blue* and its oxidation products

Alexander G. Boncheff and Mario A. Monteiro

Department of Chemistry, University of Guelph, Guelph, ON N1G 2W1, Canada

Corresponding author: **Mario A. Monteiro** (email: monteiro@uoguelph.ca)

Abstract

The Ru_xCl_y compounds that make up the widely used Ru coordination precursor, *Ruthenium Blue*, have been difficult to identify due to fast air-driven oxidation. To explore the coordination between Ru and aminated polysaccharides, the reaction between reducing glucosamine (GlcN) and *Ruthenium Blue* was investigated. A blue vibrant solution, indistinguishable from that of *Ruthenium Blue*, was obtained after reflux of GlcN/$RuCl_3$:3H_2O in ethanol, but unlike *Ruthenium Blue*, the blue colour of the reaction product persisted after prolonged exposure to air. Mass spectrometry (MALDI-ToF-MS) of the blue solution did not detect GlcN-Ru ligands. Instead, isotope patterns for singly charged Ru_xCl_y clusters were observed for $[RuCl_4]^-$, $[Ru_2Cl_6]^-$, $[Ru_2Cl_7]^-$, $[Ru_3Cl_8]^-$, $[Ru_3Cl_9]^-$, $[Ru_4Cl_{11}]^-$, and $[Ru_5Cl_{12}]^-$. Extended exposure to air led to a colour change of the blue solution to green and finally to yellow. The MS spectrum of the green solution showed lower amounts of the higher order $[Ru_4Cl_{11}]^-$ and $[Ru_5Cl_{12}]^-$, and that of the yellow solution displayed mostly $[RuCl_4]^-$. The compositions identified by MS allowed the determination of structures and corresponding electronic excitations by ab initio calculations using density functional theory. The excitation energies were matched to physically perceived colours with CIE1931 colour matching functions, with a noteworthy association of $[Ru_4Cl_{11}]^-$ to blue. We propose that the presence of the reducing monosaccharide slowed the oxidation of the Ru_xCl_y clusters in the blue solution and that the structures identified are, at least in part, constituents of *Ruthenium Blue*. These data may also be useful in the development of Ru-based reagents for catalysis and radiotherapy applications.

Key words: ruthenium, ruthenium chloride clusters, *Ruthenium Blue*, TDDFT, CIE1931, MALDI-ToF-MS

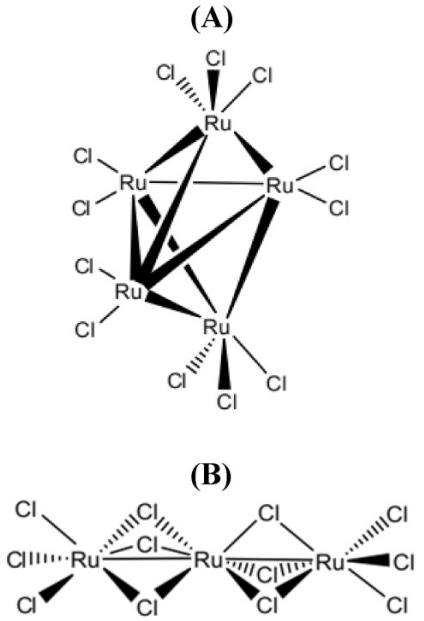
1. Introduction

Amine-containing monosaccharides, such as glucosamine (GlcN), are often found as structural components of bacterial polysaccharides (PSs). We envisaged that the coordination of ruthenium (Ru) to amine moieties[1] could be exploited in the creation of stable Ru-PS complexes to aid in the structural characterization of PSs. Our exploratory experiment focused on the coordination of free GlcN (in the reducing form) to Ru. The planned method of coordination involved the reaction of GlcN with the widely used Ru coordination precursor, *Ruthenium Blue*.

Ruthenium Blue is a versatile material used in the synthesis of Ru-containing ligands.[2] A few methods have been used in the preparation of *Ruthenium Blue* from ruthenium chloride salts. Rose and Wilkinson used hydrogen/platinum reduction in methanol,[3] whilst Mercer and Dumas used electrochemical reduction to produce the distinctive vibrant blue solution of *Ruthenium Blue*.[4] Later, a simpler method by Togano et al. employed the reflux of $RuCl_3 \cdot 3H_2O$ in ethanol under an inert atmosphere.[5] The formation of *Ruthenium Blue* can be followed by the signature colour change from the original dark yellow of the $RuCl_3 \cdot 3H_2O$ solution, to green and then blue. When exposed to air, the *Ruthenium Blue* solution quickly reverts back to green and then yellow. This high level of sensitivity to air-induced oxidation has made the study of *Ruthenium Blue* difficult with commonly used analytical techniques.

Several Ru_xCl_y compounds have been proposed to be present in *Ruthenium Blue*, in single- and multi-species solutions,[2,3] in ionic or neutral states,[4] and with Ru in various oxidation states (4+ and 2+ being the most commonly reported).[4] In 1970, Rose and Wilkinson isolated as a deep blue salt, with (o-phenylenedimethylene) bis(triphenylphosphonium) as a counter ion, a $[Ru_5Cl_{12}]^{2-}$ cluster with Ru in varying oxidation states (+4 to + 2).[3] Using data from elemental analysis and X-ray powder diffraction, Rose and Wilkinson proposed a structure for the $[Ru_5Cl_{12}]^{2-}$ cluster (Fig. 1A). One year after, Mercer and Dumas analyzed the composition of *Ruthenium Blue* and reported the presence of $[Ru_2Cl_3]^{2,3+}$, $[Ru_2Cl_4]^{1,2+}$, and $[Ru_2Cl_5]^{0,+}$ species.[4] It was proposed that a possible complex in the *Ruthenium Blue* solution was a "tri-μ-chloro bridged Ru complex in octahedral configuration with aqua ligands filling the remaining coordination sites".[4] Another notable *Ruthenium Blue* study was carried out in 1980 by Bino and Cotton,[6] who proposed a

Fig. 1. Previously proposed Ru_xCl_y clusters in *Ruthenium Blue*: (A) a $[Ru_5Cl_{12}]^{2-}$ cluster by Rose and Wilkinson[3] and (B) a $[Ru_3Cl_{12}]^{4-}$ cluster by Bino and Cotton.[6]



$[Ru_3Cl_{12}]^{4-}$ species, inferred by X-ray crystallographic data of a blue precipitate formed when $(C_2H_5)_4NCl$ was added to a solution of *Ruthenium Blue* (Fig. 1B).

In our study, no direct evidence was obtained for the coordination of GlcN to Ru, but the presence of the reducing monosaccharide appeared to have slowed down the air-induced oxidation of the blue solution product (indistinguishable from that of *Ruthenium Blue*). The unexpected stability of the blue solution product afforded enough time for its analysis by matrix assisted laser desorption ionization—time of flight—mass spectrometry (MALDI-ToF-MS). Here, we describe the Ru_xCl_y clusters detected by MALDI-ToF-MS of the blue solution product and also of its green and dark yellow oxidation products. We propose that the Ru_xCl_y clusters identified in the blue solution product are, at least in part, those that make up the coordination reagent, *Ruthenium Blue*.

2. Experimental

Synthesis of the blue solution product

The blue solution product was obtained by reacting 50 mg of D-(+)-GlcN with 1 equivalent of $RuCl_3{\cdot}3H_2O$ (calc. 73 mg) in 95% ethanol under argon. The solution was heated to reflux for 12 h, during which time the solution changed from dark yellow to green and then to a vibrant blue. The evaporation of the solvent furnished a deep blue solid. $RuCl_3{\cdot}3H_2O$ was obtained from Pressure Chemicals and D-(+)-GlcN from Sigma–Aldrich.

Mass spectrometry

For MALDI-ToF-MS analysis, the analytes were mixed with 2 mg of 3,4-dihydroxy-benzoic acid in 20% ethanol. An analyte-matrix 1:2 ratio (v/v) and 1 mL was spotted on the MALDI sample target and allowed to dry at room temperature. The analyses were performed using a MALDI-ToF-MS instrument (model Reflex III, Bruker) equipped with a 337 nm nitrogen laser. Samples were analyzed in reflectron and negative ion modes. Ion sources 1 and 2 were held at 20 and 16.35 kV, respectively. The guiding lens voltage was set at 9.75 kV and the reflector detection gain was set at 5.3 with a pulsed ion extraction at 200 ns. The nitrogen laser power was set to the minimum level needed to generate signal and avoid possible degradation of analytes, which corresponded to 15% of laser energy being used (4 mJ). The pulse duration was 9 Hz, the spot size 2 mm and the calculated energy density 100 μJ/0.1 mm.[2] A two-point external calibration was performed, using the $[M - H]^-$ (153.01 Da) and $[2M - H]^{-2}$ (447.12 Da) peaks of dehydroxybenzoic acid and the dimer of sinapinic acid, respectively, both prepared in acetonitrile-water solution (10 pmol/mL).

Computational studies

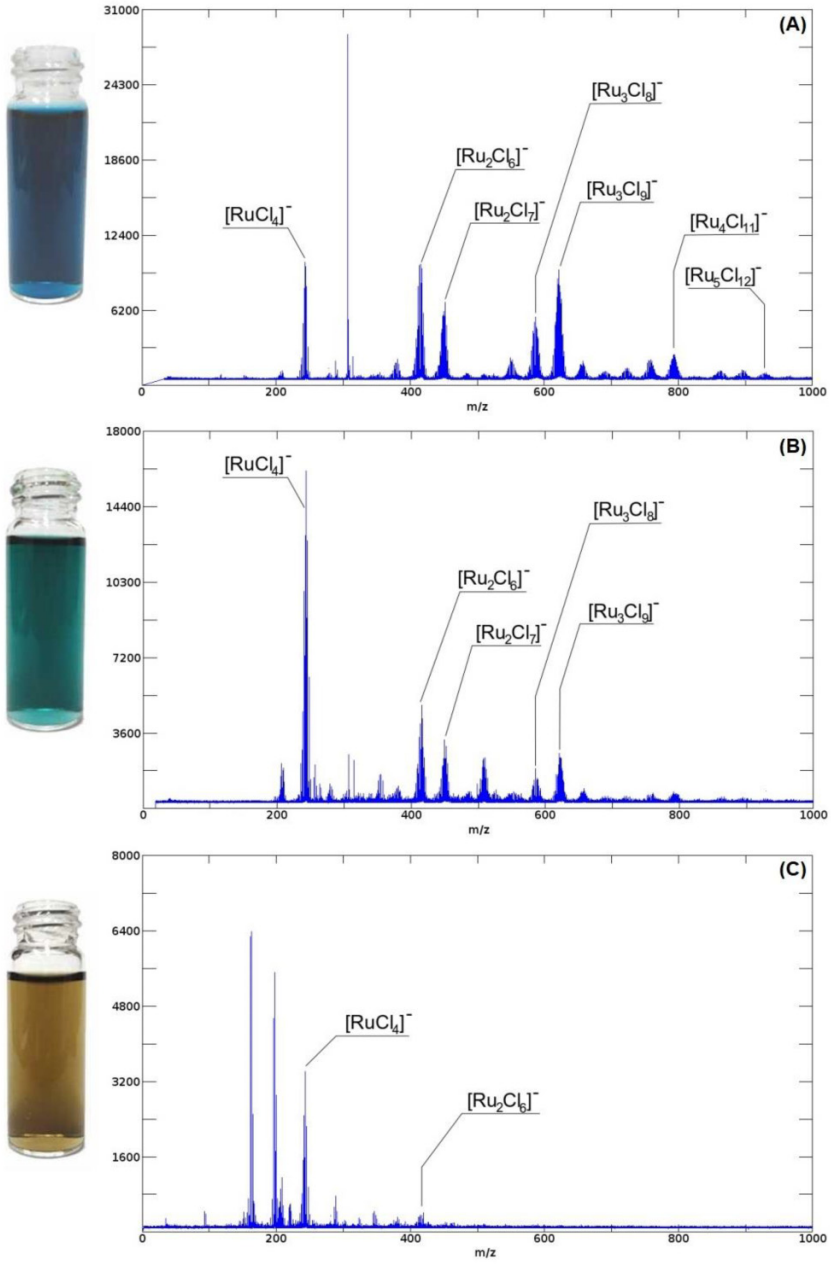
The ab initio calculations were performed using Gaussian09 Rev. A.02[7] using the density functional theory method with the PBE0 functional[8] and a combination basis set of SDD (using Stuttgart/Dresden ECPs) for Ru atoms with energy-adjusted ab initio pseudopotential with a valence contraction for Ru of 6s/5p/3d as described in Andrae et al.[9] and 6-311G(2d) for Cl atoms.[10] Vibrational frequency analysis was carried out on all optimizations to ensure true ground state geometries. Time dependent-density functional theory (TD-DFT) calculations of the geometry optimized clusters were performed to excited states in which electronic excitations of at least 300 nm were obtained. Stability tests to assure ground electronic states were performed on the clusters using the Stable function of Gaussian09. The clusters were computed using the Stable function on multiplet states to determine which multiplet set produced a stable wave function. Geometry optimizations, frequency, and TD-DFT calculations were performed with a polarizable continuum model solvent system for water.[11]

Processing of electronic excitations into UV/Vis spectra

UV/Vis spectra of the clusters were generated using a half-width, half-height of 0.305 eV. The methodology used for the generation of the CIE1931 colour space chromacity coordinates for the clusters was as follows:

TD-DFT calculations of the geometry optimized clusters were performed with sufficient excited states that ensured electronic excitations to at least 300 nm were obtained. Using the methodology from Beck,[12] the inverse spectra were integrated with each of the CIE1931 colour matching functions from 380 to 780 nm to create the red (X), blue (Y), and green (Z) CIE1931 Tristimulus values. After obtaining the Tristimulus values of X, Y, and Z, the values were summed and normalized into the chromacity coordinates with X and Y values plotted on the CIE1931 colour space metric and the corresponding data points indicated the physically perceived colours of each cluster. To generate the chromacity coordi-

Fig. 2. The blue (A), green (B), and dark yellow (C) solutions and their corresponding MALDI-ToF-MS spectra.



nates of the solutions, the UV/Vis spectra of the clusters that comprised each solution were overlapped followed by the same inversion, normalization, and integration method described above.[12] A detailed description of the methodology used for the processing of electronic excitations into UV/Vis spectra and validation experiments based on other Ru halides of known colour are described in Boncheff 2011.[13]

3. Results and discussion

The reflux of GlcN and $RuCl_3 \cdot 3H_2O$ in ethanol progressed from dark yellow, to green and lastly to a vibrant blue solution (Fig. 2A). The blue solution product was air stable, only losing its colour upon exposure to ambient atmosphere for 3–4 days, when the blue colour changed to green (Fig. 2B), which, after an additional 4–6 days, changed to dark yellow (Fig. 2C).

The MALDI-ToF-MS spectrum of the blue product (Fig. 2A) did not show any ions indicative of Ru compounds containing GlcN (no peaks containing 179 amu inclusions). However, a series of ions matching the isotopic pattern of several singly charged Ru_xCl_y species were observed, notably for: $[RuCl_4]^-$ at m/z 236–252, $[RuCl_5]^-$ at m/z 271–289 (trace amounts), $[Ru_2Cl_6]^-$ at m/z 402–428, $[Ru_2Cl_7]^-$ at m/z 437–465, $[Ru_3Cl_8]^-$ at m/z 567–603, $[Ru_3Cl_9]^-$ at m/z 602–638, $[Ru_4Cl_{11}]^-$ at m/z 773–814, and $[Ru_5Cl_{12}]^-$ at m/z 907–953. Other neighbouring m/z ions containing one or two less Cl atoms were also present. No higher m/z values were observed. Only MALDI-ToF-MS experiments in the negative ion mode showed any discernable ions of defined compositions, in which only singly charged ions were recorded. The isotopic

Fig. 3. LDI-ToF-MS spectrum of $RuCl_3 \cdot 3H_2O$ (laser ablation of $RuCl_3 \cdot 3H_2O$ with no matrix).[14]

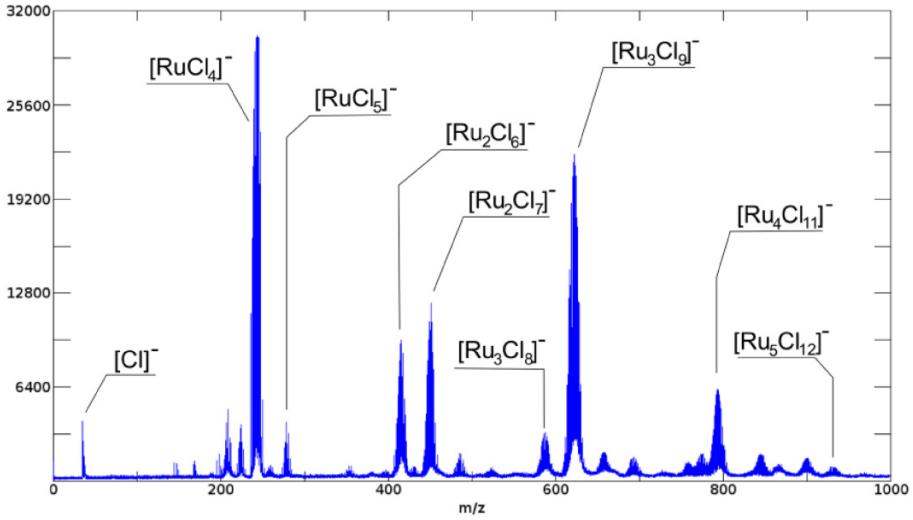
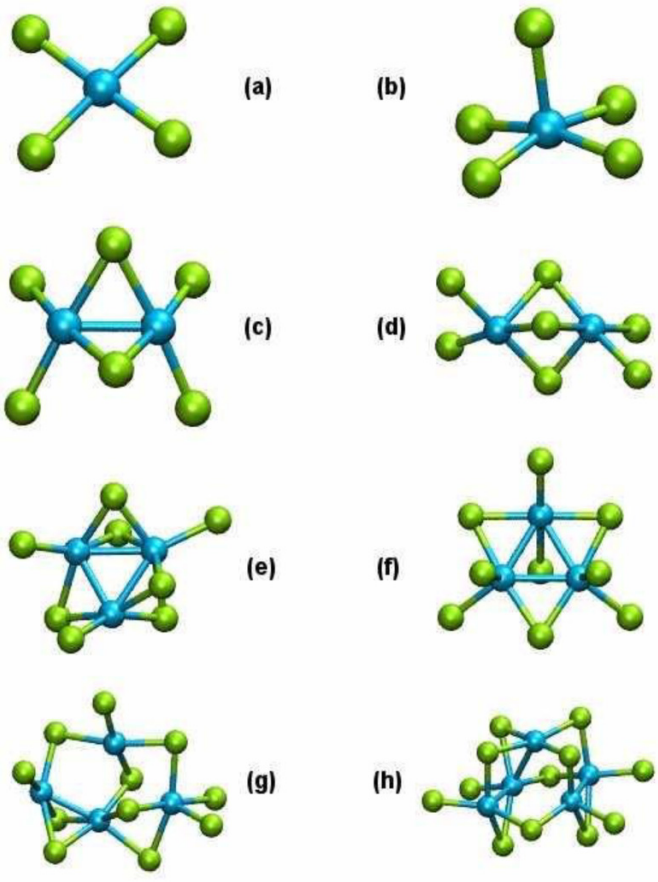


Fig. 4. Optimized structures of the Ru_xCl_y clusters identified by MALDI-ToF-MS: (*a*) $[RuCl_4]^-$, (*b*) $[RuCl_5]^-$, (*c*) $[Ru_2Cl_6]^-$, (*d*) $[Ru_2Cl_7]^-$, (*e*) $[Ru_3Cl_8]^-$, (*f*) $[Ru_3Cl_9]^-$, (*g*) $[Ru_4Cl_{11}]^-$, and (*h*) $[Ru_5Cl_{12}]^-$. Ru = blue; Cl = green.



profiles of the aforementioned Ru_xCl_y complexes observed were computationally generated and shown to match the isotopic profiles observed in the mass spectrum.[13]

The MALDI-ToF-MS spectrum of the green solution (Fig. 2B) showed a marked decrease of the $[Ru_4Cl_{11}]^-$ and $[Ru_5Cl_{12}]^-$ clusters and an increase of the $[RuCl_4]^-$ and the appearance of a specie in the $[Ru_2Cl_9]^-$ range, which suggested that the disappearance of the blue colour may involve the disintegration of the higher order $[Ru_4Cl_{11}]^-$ and $[Ru_5Cl_{12}]^-$ clusters. That of the dark yellow solution showed mainly the m/z ion corresponding to $[RuCl_4]^-$ (Fig. 2C). Interestingly, m/z ions associated with the monosaccharide, $[GlcN]^-$ at 179 and 195 $[GlcN + 16]^-$, were also seen in the mass spectrum of the dark yellow solution. GlcN-containing ligands may have indeed been present in the blue and green solutions, but were not detected under the MS experimental conditions used here.

To rule out the possibility that the Ru_xCl_y clusters observed in the MS spectra (Fig. 2) of the blue, green, and yellow solutions were not due to residual starting material, a MALDI-ToF-MS experiment was carried out solely on $RuCl_3 \cdot 3H_2O$. No Ru_xCl_y clusters were observed. However, as we have previously reported,[14] the formation of gaseous Ru_xCl_y clusters were detected when $RuCl_3 \cdot 3H_2O$ (not mixed with the matrix) was bombarded with laser. The spectrum (negative ion mode) of the laser-dissociation-ionization (LDI)-ToF-MS of $RuCl_3 \cdot 3H_2O$ (Fig. 3)[14] showed Ru_xCl_y clusters analogous to those seen in the blue solution product (Fig. 2A), but with marked differences in relative intensities, specifically $[RuCl_4]^-$, $[Ru_3Cl_9]^-$ and $[Ru_4Cl_{11}]^-$ clusters being the most prominent products from laser ablation of $RuCl_3 \cdot 3H_2O$. The LDI-ToF-MS spectrum of $RuCl_3 \cdot 3H_2O$ also furnished a strong m/z ion at 35 for Cl^- and hydroxylated $[Ru_xCl_yOH_z]^-$ ions.[14] The fact that when $RuCl_3 \cdot 3H_2O$ was mixed with the matrix, no Ru_xCl_y clusters were generated and that no higher order Ru_xCl_y clusters were seen in the green and dark yellow products, pointed to the fact that the m/z ions observed in the three MS spectra in Fig. 2 were those of compounds present in the corresponding solutions and not from ablation of residual $RuCl_3 \cdot 3H_2O$.

As described in Boncheff and Monteiro,[14] the initial input geometries of the aforementioned singly charged Ru_xCl_y com-

Fig. 5. Absorption spectra between 380 and 780 nm of (*a*) $[RuCl_4]^-$, (*b*) $[RuCl_5]^-$, (*c*) $[Ru_2Cl_6]^-$, (*d*) $[Ru_2Cl_7]^-$, (*e*) $[Ru_3Cl_8]^-$, (*f*) $[Ru_3Cl_9]^-$, (*g*) $[Ru_4Cl_{11}]^-$, and (*h*) $[Ru_5Cl_{12}]^-$.

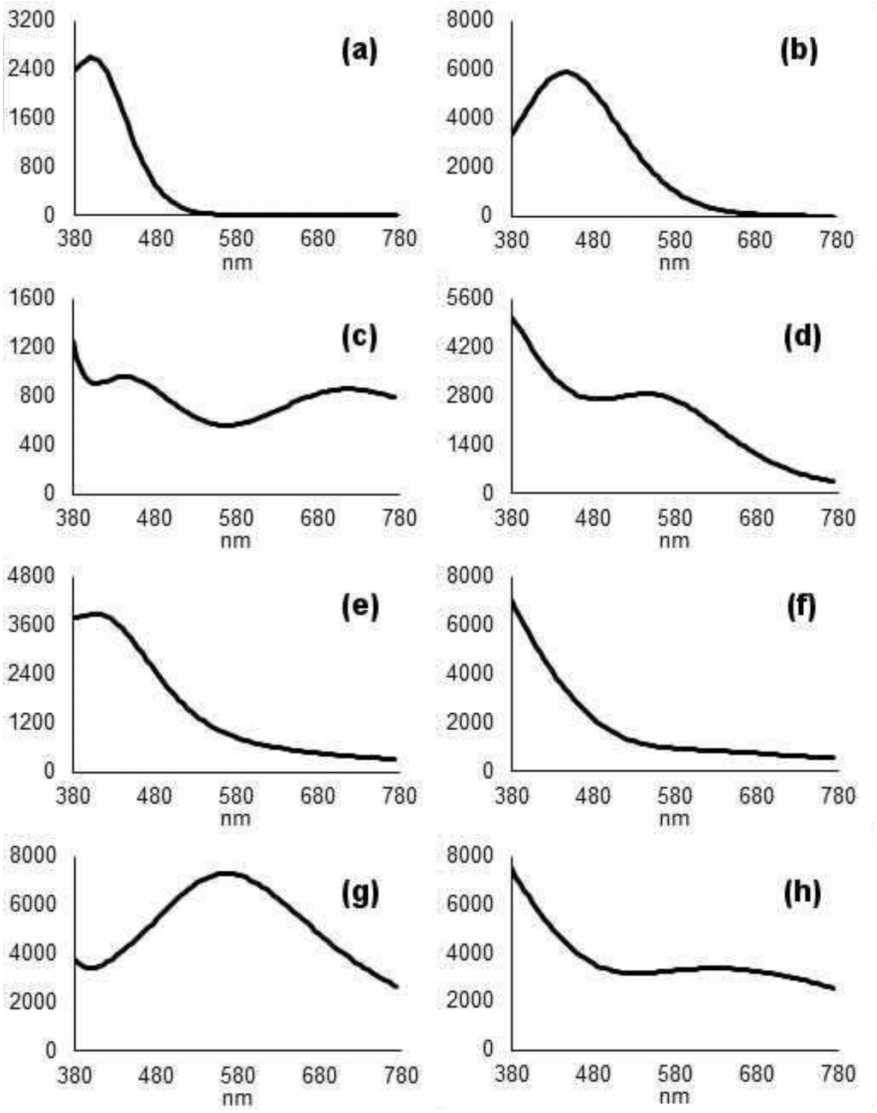


Table 1. CIE1931 chromacity coordinates for the RuxCly clusters observed in the mass spectra (Fig. 1).

Cluster	CIE1931 chromacity coordinates		Physically interpreted colour
	x	*Y*	
$[Ru_5Cl_{12}]^-$	0.351	0.370	Yellow
$[Ru_4Cl_{11}]^-$	0.223	0.116	Blue
$[Ru_3Cl_9]^-$	0.369	0.381	Yellow
$[Ru_3Cl_8]^-$	0.436	0.445	Orange
$[Ru_2Cl_7]^-$	0.365	0.345	Yellow
$[Ru_2Cl_6]^-$	0.376	0.405	Yellow
$[RuCl_5]^-$	0.491	0.463	Orange
$[RuCl_4]^-$	0.380	0.409	Yellow

pounds for the ab initio calculations were based on structures that contained Ru-Cl and Ru-Ru bonds. Possible structures were designed with Cl atoms having one or two bonds and Ru having two to six bonds. Only the structures described (Fig. 4) allowed for successful optimization. Each cluster was optimized until no virtual frequencies were observed. Re-optimization steps included (i) an increase of the size of the basis set and (ii) modification of the input structures at

Fig. 6. Coordinates of the Ru_xCl_y clusters in CIE1931 colour space.

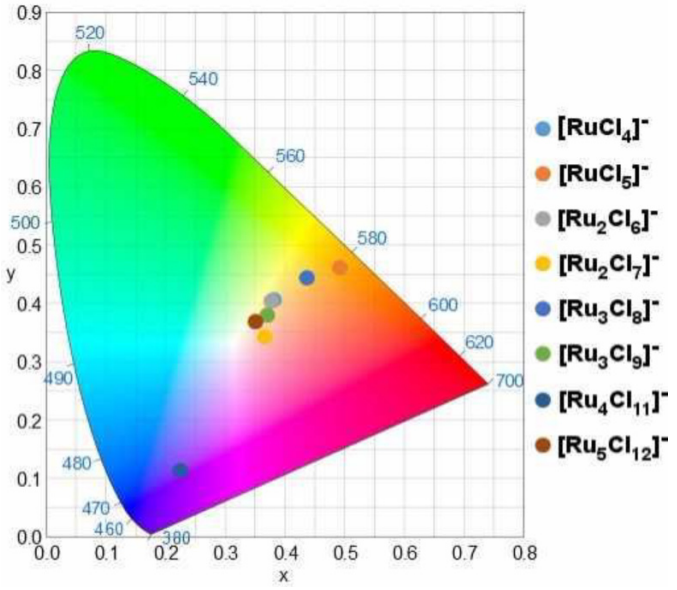
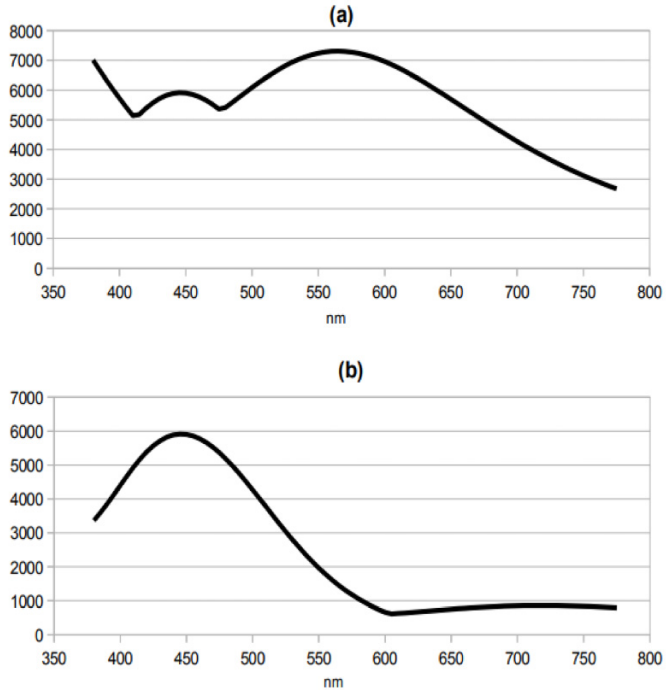


Fig. 7. Calculated UV/Vis spectra of the blue solution (*a*) and yellow solution (*b*).



the maximum point of the vibrational movement followed by optimization. The optimized structures were verified as minimized by vibrational analysis to ensure no imaginary vibrational frequencies existed and by testing the wave function stability to ensure that the geometry and multiplicity was that of the ground electronic state.[13,14] Stability tests of the Ru_xCl_y clusters showed that the singlet and doublet multiplicities were seldom the ground electronic state and higher multiplicities had to be used to obtain the electronic ground state. Figure 4 shows the output of the ab initio calculations and the geometries of the Ru_xCl_y clusters,[14] which showed the most stable spin states being: $[RuCl_4]^-$ (quartet), $[RuCl_5]^-$ (quintet), $[Ru_2Cl_6]^-$ (quartet), $[Ru_2Cl_7]^-$ (quintet), $[Ru_3Cl_8]^-$ (doublet), $[Ru_3Cl_9]^-$ (triplet), $[Ru_4Cl_{11}]^-$ (septet), and $[Ru_5Cl_{12}]^-$ (octet).

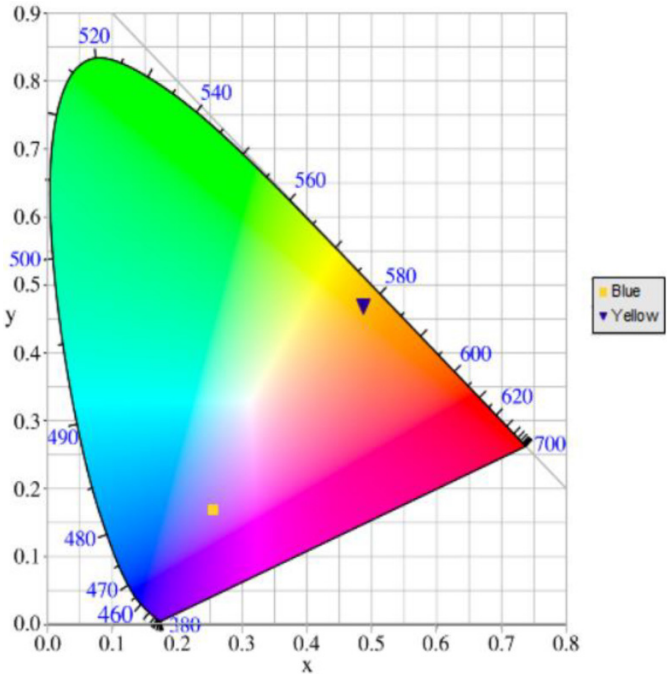
The differences in compositions observed between the three MALDI-ToF-MS spectra (Fig. 2) suggested that the corresponding solution colours were furnished by the Ru_xCl_y clusters present in each. If so, perhaps the calculation of the electronic excitations of Ru_xCl_y clusters could shed light on the source of the observed colours. Absorption spectra were then generated for the Ru_xCl_y complexes from the calculated electronic excitations. The absorption spectrum of each identified cluster is displayed in Fig. 5, and these were subsequently processed into CIE1931 colour space coordinates to represent a physically perceived colour (Table 1; Fig. 6). The spectra showed that all clusters, except $[Ru_4Cl_{11}]^-$, absorbed light in the blue/violet region, which would be physically perceived as yellow. The outlier, $[Ru_4Cl_{11}]^-$, was determined to strongly absorb light in the orange region, which would make it physically perceived as blue.

When the calculated UV/Vis spectra of the set of clusters from $[RuCl_4]^-$ to $[Ru_5Cl_{12}]^-$ were overlapped, the physically perceived colour was blue. That of the yellow solution, with the composition of mainly $[RuCl_4]^-$ and traces of $[Ru_2Cl_6]^-$, afforded a perceived colour of yellow/orange. The calculated UV/Vis spectra of the blue and yellow solutions are shown in Fig. 7 and the CIE1931 chromacity coordinates of the blue solution at $x = 0.255$ and $y = 0.167$ (for a physically perceived colour of blue), and those of the yellow solution at $x = 0.487$ and $y = 0.467$ (for a physically perceived colour of yellow/orange) can be seen in Fig. 8.

The colour change of the blue solution to green may be attributed to the decomposition of the $[Ru_4Cl_{11}]^-$ specie, the physically perceived blue cluster with the highest extinction coefficient. The proposed contribution of $[Ru_4Cl_{11}]^-$ to the blue solution colour can be seen through the comparison of the calculated UV/Vis spectra of the blue solution with that of $[Ru_4Cl_{11}]^-$ (Figs. 5*g* and 7). As $[Ru_4Cl_{11}]^-$ becomes extinct, the yellow hues generated from the remaining clusters became dominant, shifting the colour from blue to green and finally, yellow.

This MS-based study showed that a blue solution, generated by reflux of $RuCl_3{\cdot}3H_2O$/GlcN in ethanol, and its green and yellow oxidation products, varied markedly in the type of Ru_xCl_y complexes present (Fig. 2). Unlike that of the *Ruthenium Blue* solution, the blue solution product generated here in the presence of the reducing GlcN had a slower rate of oxidation when exposed to air, only losing its blue colour after 3–4 days. Undoubtedly, GlcN acted as a reducing agent that slowed the rate of oxidation of the higher order Ru_xCl_y clusters in the blue and green solutions. The role of reducing monosaccharides may thus be worth of consideration in the design of stable metal halides/ligands for use in catalysis and radiotherapies.

Fig. 8. Plot of chromacity coordinates of the blue and yellow solutions on the CIE1931 gamut.



The stability of the blue solution allowed time for MS analysis, which revealed Ru_xCl_y clusters of various compositions (Fig. 2A). The marked differences between the MS spectra of the blue, green and yellow products pointed to the fact that the observed colours were associated with the presence of specific Ru_xCl_y clusters. Based upon the colour similarity between *Ruthenium Blue* and the blue solution product, we propose that the clusters described in this work are part of *Ruthenium Blue* and that Ru_4Cl_{11} could be a compound that affords *Ruthenium Blue* its vibrant blue colour.

Acknowledgements

This work was funded by the University of Guelph. The authors thank Profs. Michael Denk and Wojciech Gabryelski for insightful discussions.

Article information

History dates

Received: 26 February 2024
Accepted: 28 May 2024
Accepted manuscript online: 8 June 2024
Version of record online: 25 September 2024

Notes

This paper is part of a Special Issue entitled Celebrating 150 Years of Chemistry at the University of Guelph.

Copyright

Data availability

Data generated or analyzed during this study are available in repository: Boncheff, A. G. Ab initio Investigations into the Geometry and Electronic Excitations of Novel Ruthenium Chloride Clusters. 2011: M.Sc. Thesis. University of Guelph. http://hdl.handle.net/10214/3141.

Author information

Author ORCIDs

Mario A. Monteiro https://orcid.org/0000-0002-6067-7772

Author contributions

Conceptualization: MAM
Data curation: AGB, MAM
Formal analysis: AGB, MAM
Funding acquisition: MAM
Investigation: MAM
Methodology: AGB, MAM
Project administration: MAM
Resources: MAM
Software: AGB
Supervision: MAM
Validation: MAM
Visualization: MAM
Writing – original draft: MAM
Writing – review & editing: MAM

Competing interests

The authors declare there are no competing interests.

References

(1) Allscher, T.; Klufers, P.; Mayer, P. *Glycoscience*, **2008**, (4), 1077. doi:10.1007/978-3-540-30429-6_24.
(2) Gilbert, J. D.; Rose, D.; Wilkinson, G. *J. Chem. Soc. (A)*, **1970**, 2765. doi:10.1039/j19700002765.
(3) Rose, D.; Wilkinson, G. *J. Chem. Soc. (A)*, **1970**, 1791. doi:10.1039/j19700001791.
(4) Mercer, E. E.; Dumas, P. E. *Inorg. Chem.* **1971**, *10*(12), 2755. doi:10.1021/ic50106a026.
(5) Togano, T.; Nagao, N.; Tsuchida, M.; Kumakura, H.; Hisamatsu, K.; Howell, F. S.; ukaida, M. *Inorg. Chim. Acta*, **1992**, *195*(2), 221. doi:10.1016/S0020-1693(00)85316-5.
(6) Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1980**, *102*(2), 608. doi:10.1021/ja00522a027.
(7) GAUSSIAN09. version A02; Gaussian, Inc.: Wallingford, C.T., 2009.
(8) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*(13), 6158. doi:10.1063/1.478522.
(9) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. *Theoret. Chim. Acta*, **1990**, *77*(2), 123. doi:10.1007/BF01114537.
(10) McLean, A. D.; Chandler, G. S. *Chem. Phys.* **1980**, *72*(10), 5639.
(11) Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct. (Theochem)*, **1999**, *464*(1–3), 211. doi:10.1016/S0166-1280(98)00553-3.
(12) Beck, M.E. *Int. J. Quan. Chem.* **2005**, *101*, 683. doi:10.1002/qua.20326.
(13) Boncheff, A. G. *Ab initio Investigations into the Geometry and Electronic Excitations of Novel Ruthenium Chloride Clusters*; M.Sc. Thesis. University of Guelph, 2011. Available from http://hdl.handle.net/10214/3141.
(14) Boncheff, A. G.; Monteiro, M. A. *Can. J. Chem.* **2011**, *89*, 511. doi:10.1139/V11-005.