

January 26, 1882.

THE PRESIDENT in the Chair.

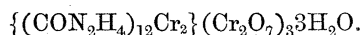
The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read:—

- I. "On a Series of Salts of a Base containing Chromium and Urea. No. 1." By W. J. SELL, M.A., F.I.C., Demonstrator of Chemistry in the University of Cambridge. Communicated by Professor G. D. LIVEING, F.R.S. Received January 13, 1882.

Various compounds of urea with metallic salts and oxides have been described by Werther and Liebig. Some of these are suggestive of an analogy between urea and ammonia, while others seem altogether anomalous. The following account of some chromium compounds of urea may help to throw some light on the nature of such compounds, for they appear to show that a very definite base is formed by a combination of urea with chromium.

When powdered and carefully dried urea is moistened with chromyl dichloride, and the mixture vigorously shaken, the temperature rises considerably, and on treating the resulting mass with water, there remains undissolved, a green crystalline powder. The nature of the green salt thus obtained is at present under investigation. It is insoluble in alcohol, ether, and chloroform. It dissolves in hot water with decomposition, another salt separating out as the liquid cools in brilliant olive-green needles, which by a second crystallisation is obtained in a pure state. The examination of this body showed it to be the dichromate of a base containing the elements of urea and chromium, and to have the formula



The dichromate thus obtained is sparingly soluble in cold, more freely in hot water, and is decomposed by boiling the solution. Its aqueous solution gives green crystalline precipitates with platinic chloride and potassium ferrocyanide, but none with ammonia.

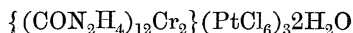
The following results were obtained on analysis:—

The numbers given refer to the dried salt, unless expressly stated to the contrary.

1. .5531 grm. gave on combustion in oxygen .2061 CO₂ and .169 H₂O.
2. .32175 grm. gave on combustion in oxygen .11865 CO₂ and .1029 H₂O.
3. .3262 grm. gave on combustion in oxygen .1189 CO₂ and .1045 H₂O.
4. .4147 grm. gave on combustion in oxygen .1499 CO₂ and .1281 H₂O.
5. .0541 grm. gave by Gottlieb's process very nearly equal volumes of CO₂ and N, weighing .01919 and .01267 respectively.
6. .35065 grm. gave by Dumas' process 62 cub. centims. nitrogen at 0° C. and 760 millims.
7. .324 grm. dissolved in water, excess of KI and HCl added, and the iodine titrated with thiosulphate, required 40 cub. centims., each cub. centim. thiosulphate = .00306 CrO₃.
8. .5253 grm. precipitated by mercurous nitrate gave .1628 grm. Cr₂O₃.
9. .9317 grm. precipitated by mercurous nitrate gave .2915 grm. Cr₂O₃.
10. The filtrate from .5253 grm. after precipitation with mercurous nitrate gave, when evaporated and ignited, .1011 grm. Cr₂O₃.
11. The mean of three concordant experiments gave on ignition 41.62 per cent. Cr₂O₃. Deducting from this the Cr existing as CrO₃, gives 10.56 per cent. Cr₂O₃ or 7.24 per cent. Cr.
12. .4985 grm. crystallised salt (dried by pressure between bibulous paper) lost .0181 grm. H₂O in vacuo over sulphuric acid, and no further loss at 105° C.

The Chloroplatinate.

When a hot solution of the dichromate is mixed with a solution of platinic chloride, and the mixture allowed to cool, the chloroplatinate crystallises out in long green silky needles. The compound is moderately soluble in hot, but very sparingly in cold water. The sparing solubility in cold water was made use of in preparing the bulk of this salt from washings and drainings from other compounds. After one or two crystallisations from hot water, the compound is obtained in a state of purity. The examination of the body led to the formula



being assigned to it.

The following results were obtained on analysis:—

The numbers given refer to the dried compound unless stated to the contrary.

1. .8698 grm. gave on combustion .2207 CO₂ and .2008 H₂O.
2. .95362 grm. ,, ,, .2331 CO₂ and .22662 H₂O.

3. .1383 grm. by Gottlieb's process gave volumes of CO_2 and N (nearly equal) weighing .034986 grm. and .0224591 grm. respectively.

4. .09505 grm. by Gottlieb's process gave volumes of CO_2 and N (nearly equal) weighing .0252056 and .0154869 respectively.

5. .2071 grm. fused with pure NaHO , acidified with HNO_3 , and titrated with AgNO_3 , using ferric sulphocyanate as indicator, required $17.85 \frac{\text{N}}{10} \text{AgNO}_3$ solution.

6. .3471 grm. burnt in a current of air, the chlorine caught by a column of pure lime and estimated gravimetrically, gave .428 grm. AgCl .

7. .3208 grm. ignited, the mixture of platinum and chromic oxide dissolved, gave .09135 Pt determined as double salt with NH_4Cl and .02364 grm. Cr_2O_3 from filtrate by precipitation with ammonia.

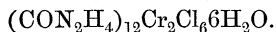
8. .07973 grm. acidified with HCl , the Pt precipitated by H_2S , and the Cr_2O_3 in filtrate after decomposition of body by boiling HNO_3 , gave .0226 Pt and .0061 Cr_2O_3 .

9. .1543 grm. acidified with HCl , and the Pt precipitated by H_2S , gave after ignition in air .0446 platinum.

10. .8408 grm. crystallised salt (dried by pressure) lost at 100°C . .014 grm. H_2O .

The Chloride.

This compound may be obtained from the original green body, or from the dichromate, by treatment with water and lead chloride. The lead chromate is filtered off, and from the filtrate the chloride is precipitated in fine silky needles by passing in hydrochloric acid gas. The compound recrystallised from warm water is deposited in long bright green prismatic crystals, having the composition



It is freely soluble in hot water, less readily in cold, the compound being decomposed by boiling its solution. Its aqueous solution is precipitated by potassium dichromate, the compound precipitated being similar in every respect to the dichromate just described. It also gives precipitates with platinic chloride and potassium ferrocyanide, but none with ammonia, until the compound has been destroyed by boiling or otherwise. The compound is almost completely precipitated from its aqueous solution by the addition of hydrochloric acid.

The following results were obtained on analysis :—

1. .7943 grm. salt gave on combustion .4036 grm. CO_2 and 3369 grm. H_2O .

2. .48795 grm. titrated with $\frac{\text{N}}{10} \text{AgNO}_3$ required 28.16 cub. centims.

3. .1477 grm. (another sample precipitated by HCl) titrated with $\frac{N}{10}$ AgNO₃ required 8.6 cub. centims.

4. .4274 grm. ignited left .062 grm. Cr₂O₃.

5. .5382 grm. crystallised salt dried by pressure lost at 104° C. .05025 grm. H₂O.

Theory.			Analysis.				
			1.	2.	3.	4.	5.
		Percentage.					
C ₁₂	144	13.87	13.85				
H ₄₈	48	4.62	4.70				
N ₂₄	336						
O ₁₂	192						
Cr ₂	104.8	10.09	9.94	
Cl ₆	213	20.52	..	20.48	20.67		
	1037.8						
6H ₂ O	108	9.42	9.33
	1145.8						

The Sulphate.

This compound is readily obtained from the preceding, by the action of silver sulphate. The silver chloride is filtered off, and the solution concentrated at a gentle heat or in vacuo. If the warm solution of the chloride be rubbed up in a mortar with the proper quantity of silver sulphate, a crop of crystals of this compound is deposited after filtration, on cooling, in short dark green prisms. The crystals have the composition (CON₂H₄)₁₂Cr₂(SO₄)₃10H₂O.

The following results were obtained on analysis:—

1. .385 grm. salt, dried by pressure between bibulous paper, lost at 105° C. .0538 grm. water, and gave, when dissolved and the sulphuric precipitated by BaCl₂, .208 grm. BaSO₄.

Theory.		Analysis.	
	Percentage.		
C ₁₂	144		
H ₄₈	48		
N ₂₄	336		
O ₁₅	240		
Cr ₂	104.8		
(SO ₃) ₃	240	18.56	18.54
10H ₂ O.....	180	13.92	13.98
	1292.8		

The Nitrate.

This compound is readily obtained from the dichromate or chloride by nitrate of silver. If the solutions used are warm and fairly concentrated, a good crop of crystals is deposited on cooling after filtration. The salt separates from the warm saturated solution, or by spontaneous evaporation in large, well-defined, dark green prisms, which are anhydrous, and may be represented by the formula $(\text{CON}_2\text{H}_4)_{12}\text{Cr}_2(\text{NO}_3)_6$. The following determinations were made:—

1. .449 grm. crystallised salt lost no appreciable quantity of water at 104°C ., and is therefore anhydrous.
2. .0908 grm. gave 25.67 cub. centims. nitrogen at 0° and 760 millims.
3. .378 grm. ignited left .0493 Cr_2O_3 .
4. .22175 ,, .02895 ,,

Theory.				Analysis.		
				2.	3.	4.
Percentage.						
C_{12}	144					
H_{48}	48					
N_{30}	420	35.09		35.46		
O_{30}	480					
Cr_2	104.8	8.75		..	8.94	8.95
	<u>1196.8</u>					

The Hydroxide.

A mixture of the dichromate, cold water, and a slight excess of pure precipitated lead hydroxide, rubbed together in a mortar, the lead chromate removed by filtration and any excess of lead by a drop of the dichromate, yields a bright green strongly alkaline solution. This solution appears to contain the hydroxide of the same base as the salts just described, for they are easily obtained from it by suitable reagents. A precisely similar solution may be obtained from the sulphate by means of barium hydroxide. The compound, however, is slowly decomposed in the cold, more rapidly on heating, the solution losing its alkalinity, chromic hydroxide separating out and urea remaining in solution. If the green aqueous solution be mixed with alcohol, most of the hydroxide is deposited as a light green precipitate, which may be collected, redissolved in water, and reprecipitated by alcohol unchanged. It is, however, difficult to prevent some decomposition occurring, especially in drying. On this account, I have not at present succeeded in isolating it in a sufficiently pure state for analysis.

Up to the present time, no compounds of chromium with ammonia have been described, which are analogous in composition to those forming the subject of this paper. The metal cobalt, however, forms with ammonia the base of Frémy's well-known series of luteocobaltic salts, to which these compounds bear a marked resemblance. Comparing the compounds at present analysed with the corresponding luteocobaltic salts:—

New Series.		Luteocobaltic Salts.
$\{(\text{CON}_2\text{H}_4)_{12}\text{Cr}_2\}(\text{Cr}_2\text{O}_7)_3\cdot 3\text{H}_2\text{O}$	$\{(\text{NH}_3)_{12}\text{Co}_2\}(\text{Cr}_2\text{O}_7)_3\cdot 5\text{H}_2\text{O}$
$\{(\text{CON}_2\text{H}_4)_{12}\text{Cr}_2\}(\text{PtCl}_6)_3\cdot 2\text{H}_2\text{O}$	$\{(\text{NH}_3)_{12}\text{Co}_2\}(\text{PtCl}_6)_3\cdot 6\text{H}_2\text{O}$
$\{(\text{CON}_2\text{H}_4)_{12}\text{Cr}_2\}\text{Cl}_6\cdot 6\text{H}_2\text{O}$	$\{(\text{NH}_3)_{12}\text{Co}_2\}\text{Cl}_6$
$\{(\text{CON}_2\text{H}_4)_{12}\text{Cr}_2\}(\text{SO}_4)_3\cdot 10\text{H}_2\text{O}$	$\{(\text{NH}_3)_{12}\text{Co}_2\}(\text{SO}_4)_3\cdot 5\text{H}_2\text{O}$
$\{(\text{CON}_2\text{H}_4)_{12}\text{Cr}_2\}(\text{NO}_3)_6$	$\{(\text{NH}_3)_{12}\text{Co}_2\}(\text{NO}_3)_6$

Several other compounds are in course of preparation or analysis, and will form the subject of a further communication.

I am greatly indebted to my friend and former pupil, Mr. C. T. Heycock, B.A., for much valuable aid in the analysis of these complicated compounds.

I desire also to express my thanks to Professor Living for much valuable advice and assistance.

II. "On the Spectrum of Water. No. II." By G. D. LIVING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge.
Received January 14, 1882.

In our former communication on the subject of the water spectrum ("Proc. Roy. Soc.," vol. 30, p. 580) we stated that the spectrum we then figured did not by any means exhaust the spectra of flames we had observed, but it was as much as we had at that time been able to trace to water as its cause. We had, in fact, noticed in the spectrum of coal-gas and hydrogen-flames a still more refrangible but less intense series of lines; and we have since observed that this second series is produced under the same circumstances as the first, and we therefore ascribe it to the same cause, namely, the incandescent vapour of water. It is easily produced not only by the flames just mentioned, but by the arc of a De Meritens machine when a current of steam is passed into it, and by the spark of an induction coil without jar in moist air or other moist gas. When a large coil and jar are used it almost or wholly disappears.

The accompanying figure is drawn from a photograph of the spectrum of an oxyhydrogen flame; and the wave-lengths marked on