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COLOUR AND CHEMICAL CONSTITUTION

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COLOUR AND CHEMICAL CONSTITUTION.

PART VII.—SPECTRA OF SOLID COMPOUNDS OF COBALT, NICKEL,
MANGANESE, AND URANIUM.

BY JAMES MOIR, M.A., D.Sc., F.I.C.

The main result of the earlier part of this work is the demonstration of the fact that simple coloured substances can have their colour altered by "loading" the molecule either internally or by combination with a non-ionising solvent. This phenomenon being very regular in the organic field, it became of interest to see whether it could be traced in the coloured compounds of such metals as give derivatives possessing a definite spectrum. Cobalt was first chosen because the striking spectrum of cobalt-glass suggested that non-ionised cobalt compounds would all have characteristic spectra.

I. SPECTRA OF THE COMPOUNDS OF COBALT.

The spectrum of cobalt salts dissolved in water is not striking; it is the same for all salts when a dilute solution is examined in a thick layer, and consists of a single very broad indefinite band with its centre near λ 495, this being due to the hydrated cobalt ion. Examination of partly non-ionised cobalt solutions in thin layers of strong solutions show small differences due to partial combination with the salt ion, this leading to a higher molecular weight or volume and therefore to a "loaded" vibration with higher wave-length. The centre of the broad band is near λ 505 for both the chloride and nitrate and near λ 510 for the acetate when a strong solution is examined in a thin layer. When the nitrate is fused without the addition of water the band-centre is raised to λ 510, which thus appears to be the wave-length of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{Aq}$ in the non-ionised condition.

Solution of CoSO_4 in hot conc. H_2SO_4 is blue, with the band-centre raised as high as λ 575; on cooling this turns pink and has the band at λ 545. On the loading hypothesis the latter is probably due to $\text{Co}(\text{HSO}_4)_2$ and the blue form to a compound of this with H_2SO_4 . The change of pink cobalt compound to blue by heat is a general phenomenon (whether

water is present or not), and appears to be due to increase of molecular weight or volume by combination with the environing molecules. Curiously enough the nitrate and fluoride form exceptions and scarcely change at all with heat; and cobalt glass and cobalt phosphate would probably be pink at low temperatures. Some examples of this change from pink to blue may now be discussed.

a. Cobalt chloride, which in dilute solution shows the ion band at λ 495, in the solid state has the band shifted a little higher but of the same character. If the solution is boiled or treated with a little HCl two remarkable *very narrow* bands develop in the orange and the solution becomes violet. These bands are at $\lambda\lambda$ 607 and 621. Further addition of HCl, probably leading to the formation of HCoCl_3 , causes the solution to turn blue, when the original band at about λ 505 disappears and a very strong absorption with centre at λ 700 in the far red comes up, accompanied by another of centre λ 661 and a faint one at λ 640. In intermediate stages all five bands are visible, viz. the three just mentioned and the hair lines at $\lambda\lambda$ 607 and 621. When a trace of cobalt salt is dissolved in a large excess of conc. HCl the solution is greenish-blue (quite a sensitive test for cobalt), and the spectrum shows the bands at $\lambda\lambda$ 661 and 700 coalesced into one band going from λ 655 to λ 705, *i. e.* starting at the C line of the sun and going half-way to the red end. Probably it is H_2CoCl_4 which gives this spectrum. This band is of course wider if strongly-coloured solutions are used and a sixth band near λ 530 then appears.

b. Cobalt bromide does not change appreciably with heat or with considerable additions of HBr, but if dissolved in HBr (1.38 sp. gr.) and then heated the pink solution turns green, and this does not go back at once on cooling. The spectrum of the green solution is remarkable, consisting of four bands in the red, viz. a pair at $\lambda\lambda$ 637 and 662 (probably due to HCoBr_3 , since they are narrow and analogous to those attributed to HCoCl_3 at $\lambda\lambda$ 607 and 621), and a pair of broader strong bands with centres at $\lambda\lambda$ 694 and 735, probably due to H_2CoBr_4 (*cf.* $\lambda\lambda$ 661 and 700 in H_2CoCl_4). In deeply-coloured solutions the whole red end from λ 680 to λ 760 is absorbed. The band at λ 735 is a most exceptional one, being, I think, the only known narrow absorption-band in the far red in any substance; direct sunlight or similar intense light is necessary to enable it to be seen, and a violet filter should be used to protect the eye from the glare of the adjacent orange light.

c. Cobalt iodide changes from pink with the utmost difficulty, but a yellow-green film was obtained on drying an HI solution of CoI_2 , which had a marked band at λ 694. This probably corresponds to HCoI_3 and to λ 621 in HCoCl_3 and λ 662 in HCoBr_3 . A very dark brown, practically opaque, phase is produced on further drying, which could not be obtained thin enough for spectroscopy.

d. Cobalt-glass and its analogues.—This blue glass has three marked absorption-bands with centres at $\lambda\lambda$ 541, 589 and 652. The spectrum of the *cobalt borax-bead* is similar, but the bands are lower down (mol. wt. of cobalt borate less than that of cobalt silicate), the centres being at $\lambda\lambda$ 527, 577 and 641. A third spectrum of this class is given by cobalt dissolved in hot fused metaphosphoric acid ($\text{Co}(\text{PO}_3)_2$ in HPO_3) which has band-centres at $\lambda\lambda$ 533, 582, and about 640. This turns pink on cooling and loses the spectrum just described. The middle band is much stronger than the others in all cases. The blue solution of cobalt in very strong potash, containing $\text{Co}(\text{OK})_3$, gives a fourth spectrum of this class, the centres being at $\lambda\lambda$ 530, 579 and 638. The purple solution from cobalt, potash and sugar contains only two bands, the chief one being at λ 592, the other, at λ 490, being probably only that of cobalt hydrate. If glycerol be used instead of sugar the solution is blue and the bands are at $\lambda\lambda$ 585 and 640, *i. e.* very like the glass. Cobalt ammonium phosphate in ammonia is purple and the bands are at $\lambda\lambda$ 598 and 629.

Another and more remarkable blue cobalt solution is the double potassium sulphocyanide K_2CoScy_4 . This, when extracted into alcoholic ether, has sharp bands at $\lambda\lambda$ 579 and 621, and when in amyl alcohol or amylacetate has the bands at $\lambda\lambda$ 581 and 626.

The cobaltamines with trivalent cobalt have no characteristic spectra.

II. SPECTRA OF THE NICKEL COMPOUNDS.

Although nickel chloride gives a characteristic spectrum, none of the other compounds show anything definite. This is probably because the effect of loading the molecule is to shift the absorption-bands right off the spectrum. $\text{NiCl}_2 \cdot \text{Aq}$ has two absorption-bands with centres at about $\lambda\lambda$ 652 and 690 and a strong narrow transmission between them (at about λ 675). This transmission survives in strong solutions in which the bands have broadened so as to cut off nearly all the rest of the red.

III. THE SPECTRUM OF THE PERMANGANATES.

Dilute solutions of permanganates, it is well known, give an absorption-spectrum containing five bands which appear to be equally spaced. Two of these, the second and third, are much stronger than the others, and by using stronger solutions the author has been able to observe two more farther down in the violet, making seven bands in all. The author has also succeeded in expressing their rhythmic character by a mathematical formula,

viz. $\lambda = \frac{10^7}{1750 + 78N}$, which, by taking N to be successively 0, 1, 2, 3, 4, 5, and 6, gives seven values of λ agreeing within experimental error with the

observed wave-lengths of the absorption-centres, viz. 572, 547, 525, 504, 485, 468 and 451 (observed 572, $546\frac{1}{2}$, $524\frac{1}{2}$, 503, 486, 469 and 454). The reflection spectrum of solid KMnO_4 contains emission-bands at 577, 552, 530, etc., which evidently correspond to the non-ionised KMnO_4 of slightly higher molecular weight or volume than the ion MnO_4^- to which the ordinary absorption bands belong.

IV. SPECTRA OF URANIUM COMPOUNDS.

The uranyl compounds in solution exhibit a spectrum which is a sort of imitation or continuation of the permanganate spectrum, consisting of five bands equally spaced in the blue. For the UO_2^{++} ion (thick layer of dilute solution) the positions of the five absorption-centres are $\lambda\lambda$ 473, 459, 446, 433 and 420, the central one being strongest. The effect of "loading" was studied by examining *solid* uranium salts by transmitted light, excluding fluorescence by means of a black cover. Uranyl acetate (+3Aq) gave the readings $\lambda\lambda$ 476, 464, 445, 432 and 422. Basic uranyl acetate (orange) gave $\lambda\lambda$ 487, 471, 459, 449 and 440. Hydrated uranyl chloride gave only $\lambda\lambda$ 483 and 467. Hydrated uranyl nitrate gave $\lambda\lambda$ 486, 469 and 455, which remained unchanged even after melting the crystals and heating for some time.

Uranyl bisulphate in conc. H_2SO_4 (strong thin layer) and uranyl metaphosphate in HPO_3 both had the same four bands, at $\lambda\lambda$ 492, 475, 458 and 438; uranyl perchlorate in conc. HClO_4 had the bands at $\lambda\lambda$ 488, 471, 456 and 443; in the solid state this substance gave bands at about $\lambda\lambda$ 506, 490 and 470, and possibly a higher and a lower one; finally, solid natural autunite (from Madagascar*) gave $\lambda\lambda$ 514 faint, 500, 485, 470 and 456.

The latter two show great loading effect as a result of their much greater molecular size, and, speaking generally, the change in position of the bands follows the molecular weight qualitatively though not proportionally.

In fact, the change in wave-length appears all through to be roughly proportional to the 6th root of the molecular weight. Thus for autunite, as

compared with the ion UO_2^+ , the ratio of the molecular weights is $\frac{914}{540}$, of

which the 6th root is 1.091: now the five ratios $\frac{514}{473}$, $\frac{500}{459}$, $\frac{485}{446}$, $\frac{470}{433}$ and $\frac{456}{420}$ have all an average of 1.089 within the experimental error.

A similar state of affairs holds for uranyl perchlorate if we assume one mol. of Aq. and make the line λ 506 correspond with the *second* line of UO_2^{++} , viz. 459: the ratios of all the lines agree with the 6th root of the ratio of the molecular weights.

* $\text{Ca}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{Aq.}$

† Multiplied by 2.

In the case of cobalt the homologous lines $\lambda\lambda$ 621, 662 and 694, seen respectively in the acid chloride, bromide, and iodide, have ratios which are almost exactly the same as the 8th root of the ratios of the molecular weights.

In the phthaleins, where the substituents are singly-linked carbon atoms, it is the 4th root of the ratio of the molecular weights which agrees with the ratio of the absorption wave-lengths, but the halogen-derivatives do not follow this rule.

I do not yet know if it is more than a coincidence that these roots, 6, 8 and 4, are the same as the valencies (periodic place) of uranium cobalt and carbon.

NOTE ON URANOUS (TETRAVALENT) COMPOUNDS.

These are blue-green and have a striking spectrum. The band-centres of the U^{++++} ion are: $\lambda\lambda$ 688 and 673 (hair-lines), 650 (very strong), 553, 496 and 440. $U(PO_3)_4$ in solid HPO_3 has the bands $\lambda\lambda$? 700, 689, 670 (strong), 629, ? 580 and 545.