pressure over sulfur trioxide concentrations from 5.10 to 22.02%. Two stable solid phases have been found to exist in this range: $Al_2O_3\cdot SO_3\cdot 6H_2O$ and $Al_2O_3\cdot 2SO_3\cdot 11H_2O$. Equilibrium has been attained over the entire region studied. The investigation has given evidence that many basic aluminum sulfates reported in the literature are not stable chemical individuals at 60° and atmospheric pressure.

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Double Alkali Chromates of Some of the Transition Elements

BY WINSLOW H. HARTFORD AND KEITH A. LANE

An important group of compounds of this type was first described by Gröger.[1] Although variously formulated in subsequent literature, they possess the oxide formula $M^{i}_{2}O\cdot 4M^{ii}O\cdot 4CrO_3\cdot 3H_2O$. Salts were described where M^{i} and M^{ii} were potassium and zinc, potassium and copper, potassium and cadmium, potassium and cobalt, NH_4 and cadmium, and NH_4 and cobalt, respectively. The "zinc yellow" of commerce has recently been identified as being composed principally of $K_2O\cdot 4ZnO\cdot 4CrO_3\cdot 3H_2O$; the situation having been clarified by published analyses[2,3] and preparation of the compound in well-defined crystals by Tarr, Darrin and Tubbs.[3] These workers also prepared the sodium zinc salt in a state of purity by reaction of sodium tetrachromate solution on a suspension of zinc oxide, a method yielding a finely divided product suitable for use as a pigment,[4] but not entirely free from zinc oxide or susceptible of easy examination to determine uniformity.

Because of the probability of preparing additional compounds of this general type, attempts were made to prepare unlisted compounds of sodium, ammonium and potassium with cadmium, cobalt, copper, nickel and zinc.

Experimental

All compounds were first investigated by dropwise addition of the alkali chromate solution to a boiling solution of the appropriate metal oxide or carbonate in excess chromic acid. Products were filtered off, washed with cold water, alcohol and ether, and dried in warm air. This method was modified on occasion by the addition of alkali nitrates or acetates to the heavy metal oxide–chromic acid solution to change concentrations of alkali ion.

Further investigation of conditions of precipitation was made by addition of alkali dichromates to heavy metal acetates to provide a buffered solution, and also by the dropwise addition of both alkali chromate and heavy metal dichromate solution to a solution which could be maintained at desired values of hexavalent chromium, alkali salt, heavy metal and hydrogen-ion concentration.

The following well defined, previously undescribed compounds were obtained:

Sodium Copper Chromate.—Dropwise addition of 3.3 molal sodium chromate solution to a boiling solution of 40 g. of cupric oxide and 150 g. of chromium trioxide in 200 g. of water gave a maroon crystalline precipitate. Precipitation started at a *p*H of about 1 and was complete at a *p*H of 4, when substantially all the copper was precipitated and no further precipitate was noted on further addition of chromate. The product was mostly crystalline aggregates although an occasional diamond-shaped single crystal 0.005 to 0.01 mm. in length, was seen. Calculated for $Na_2O\cdot 4CuO\cdot 4CrO_3\cdot 3H_2O$: Na_2O, 7.43; CuO, 38.15; CrO_3, 47.94; H_2O, 6.47. Found: Na_2O, 7.31; CuO, 38.27; CrO_3, 47.68; H_2O, 6.34; density, $d^{30}{}_4$ 3.57.

To check further the chemical individuality of this material, analyses were made of precipitate removed from the reaction mixture as the precipitation progressed. The following results were obtained at various *p*H values:

*p*H	CrO_3 content of precipitate, (theory 47.94)
~1	47.42
2.52	48.98
3.56	47.53
3.97	47.38

All precipitates were similar in color and crystalline appearance to the product described above.

The product was also obtained by dropwise addition of two solutions, one containing 86 g. of cupric carbonate (57% CuO) and 150 g. of chromium trioxide in 400 g. of water, the other 3.9 molal sodium chromate solution, to a boiling solution of 250 g. of sodium dichromate dihydrate in 500 g. water. When the *p*H was such that Cu^{++} was present in the solution in appreciable quantity, as shown by a brownish tinge to the solution, crystals were readily obtained, which were identical with those obtained above, but much larger in size. Single crystals were obtained having a length of 0.16 mm. when the *p*H was maintained between 2.6 and 3.1. The crystals are maroon, highly refracting, transparent, tabular, and diamond shaped, with an acute angle of about 63° as measured on the microscope stage. They contained 47.51% CrO_3.

When concentration conditions are such that Cu^{++} is not present in solution, a brown amorphous precipitate is obtained, much lower in CrO_3 and sodium content. This is apparently the previously reported[5] hydrous basic chromate, $3CuO\cdot CrO_3\cdot xH_2O$. It dissolves immediately from the double salt crystals when the *p*H is lowered and the Cu^{++} concentration increased.

The reaction as described above was also carried out at room temperature. The product consisted of smaller crystals than the above, but still was similar in appearance and analysis; $CrO_3 = 47.38\%$.

Sodium Cobalt Chromate.—Dropwise addition of 3 molal sodium chromate solution to a boiling solution of 59.5 g. of cobaltous carbonate and 150 g. of chromium trioxide in 300 g. of water yielded a crop of gray-black

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[1] M. Gröger, *Sitzber. Akad. Wien*, **112**, 263 (1903); **113**, 155 (1904); *Z. anorg. Chem.*, **49**, 196 (1906); **58**, 412 (1908).

[2] A. A. Brizzolara, R. R. Denslow and S. W. Rumbel, *Ind. Eng. Chem.*, **29**, 656 (1939).

[3] O. F. Tarr, M. Darrin and L. G. Tubbs, THIS JOURNAL, **66**, 929 (1944).

[4] O. F. Tarr and M. Darrin, "Process of Preparing Zinc Yellow Pigments," U. S. Patent 2,415,394, February 4, 1947.

[5] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, p. 261, Longmans, Green and Co., New York, 1931.

crystalline aggregates. Precipitation started at a *p*H of about 2 and was complete at about 4.5, the product being uniform in appearance throughout the precipitation. No further precipitation occurred on addition of more chromate. Calculated for $Na_2O{\cdot}4CoO{\cdot}4CrO_3{\cdot}3H_2O$: Na_2O, 7.60; CoO, 36.75; CrO_3, 49.03; H_2O, 6.62. Found: Na_2O, 7.50; CoO, 36.94; CrO_3, 48.98; H_2O (difference), 6.58; density, d^{30}_4 3.43.

On addition of 3 molal sodium chromate solution and a solution of 45 g. of cobaltous carbonate and 112 g. of chromium trioxide in 400 g. of water to a boiling 1 molal solution of sodium dichromate dihydrate, precipitation occurred at a *p*H of about 4 and black individual crystals formed which later agglomerated. These crystals were identical in appearance to those previously obtained, but were considerably larger, reaching a length of 0.02 mm. Individual crystals were diamond-shaped, tabular, and red-brown by transmitted light. The acute angle was measured as 62°; analysis, 48.63% CrO_3.

Ammonium Zinc Chromate.—Dropwise addition of saturated ammonium chromate to a boiling solution of 40.7 g. of zinc oxide and 150 g. of chromium trioxide in 600 g. of water gave orange-yellow crystalline aggregates at *p*H 2 and precipitation of zinc was virtually complete at *p*H 4.5. A slight amount of non-crystallized material was precipitated on further addition of ammonium chromate. Analysis of the product indicated a higher proportion of ammonia than calculated for the 1:4:4:3 salt, as follows:

	Calculated for $(NH_4)_2O{\cdot}4ZnO{\cdot}4CrO_3{\cdot}3H_2O$	Found	Calculated for $3NH_3{\cdot}4ZnO{\cdot}4CrO_3{\cdot}3H_2O$
NH_3	4.09	6.47	6.15
ZnO	39.14	38.37	39.18
CrO_3	48.10	48.22	48.16
H_2O	8.67	6.94 (diff.)	6.51

Other samples taken at various stages during the precipitation contained 48.47% and 47.93% CrO_3, and were identical in appearance. The crystals showed an occasional hexagonal plate-like single crystal, 0.005 to 0.025 mm. in diameter; density, d^{30}_4 3.09. These hexagonal plates were reported by Tarr, Darrin and Tubbs[3] to constitute a small percentage of their preparation of $(NH_4)_2O{\cdot}4ZnO{\cdot}4CrO_3{\cdot}3H_2O$ and account for the high values reported by them for the ammonia content.

Dropwise addition of saturated ammonium chromate and a solution of 81.4 g. of zinc oxide and 200 g. of chromium trioxide in 250 g. of water to 2 molal ammonium bichromate buffered to a designated *p*H with ammonium hydroxide gave a similar product at *p*H values between 3.0 and 5.5, orange-yellow hexagonal plates being observed as before. When the precipitation was conducted at *p*H 6.0 the material became lighter yellow and less crystalline in appearance, and the analysis changed;

*p*H of precipitation	NH_3, %	CrO_3, %	Molecular ratio
3.0	6.07	47.46	0.753
4.5	6.18	48.16	.755
6.0	7.93	49.70	.939
Theory	6.15	48.16	.750

Ammonium Cobalt Chromate. Dropwise addition of saturated ammonium chromate solution to a boiling solution of 59.5 g. cobaltous carbonate and 150 g. chromium trioxide gave gray-black crystalline aggregates in which no single crystals were detectable. The first precipitate formed was similar in appearance to the final product which was obtained at a *p*H of about 4. At this point, further addition of ammonium chromate produced no additional precipitation. Calculated for $3NH_3{\cdot}4CoO{\cdot}4CrO_3{\cdot}3H_2O$: NH_3, 6.35; CoO, 37.24; CrO_3, 49.70; H_2O, 6.71. Found: NH_3, 6.10; CoO, 37.33; CrO_3, 49.97; H_2O (diff.), 6.60; density, d^{30}_4 2.95.

Other Results: Ammonium Cadmium Chromate.—Addition of ammonium chromate solution to boiling cadmium dichromate solution gave a crystalline precipitate identified as the previously reported[1] salt $(NH_4)_2O{\cdot}4CdO{\cdot}4CrO_3{\cdot}3H_2O$. Calculated: NH_3, 3.34; CrO_3, 39.23. Found: NH_3, 3.32; CrO_3, 39.19. Diamond-shaped, tabular yellow crystals were obtained with an acute angle of 64°. Precipitation of cadmium was incomplete at *p*H 5. Further treatment of the mother liquors with dilute ammonium hydroxide gave crystalline products containing larger amounts of NH_4 and Cd, but not conforming to any simple formula. This reaction was investigated to determine whether the previously unreported $3NH_3{\cdot}4CdO{\cdot}4CrO_4{\cdot}3H_2O$ would form.

Sodium Cadmium Chromate.—Dropwise addition of sodium chromate to a solution of cadmium dichromate produced yellow crystals, free from sodium, which are presumably cadmium chromate containing a trace of basic salt. Calculated for $CdCrO_4$: CrO_3, 43.7. Found: CrO_3, 42.6. Reversal of the order of addition, or precipitation in the presence of large quantities of sodium ion, failed to give any products containing sodium.

Ammonium Copper Chromate.—Precipitation by dropwise addition of ammonium chromate solution to a boiling copper dichromate solution gave a voluminous brown apparently amorphous precipitate conforming approximately to the analysis $3NH_3{\cdot}4CuO{\cdot}4CrO_3{\cdot}3H_2O$. By precipitating in the presence of excess ammonium ion, dense, uniform crystalline precipitates were formed, in which, however, the composition varied considerably from that of the double salt. Addition of both ammonium chromate and copper dichromate solution to ammonium dichromate solution gave similar results. Although some products approximated the desired composition and appeared uniform under the microscope, it was found that well defined crystals were absent, and that minor variations in precipitation procedure produced substantial change in the analysis. In previous experiments, the appearance of a second phase was readily detected by microscopic examination. The uniformity of the precipitate under careful observation indicates, but does not prove, the absence of a mechanical mixture of two or more compounds. It was therefore concluded that the precipitates were either adsorption products, or more probably solid solutions of the type in which an excess or deficiency of certain components may be held within the lattice giving a non-stoichiometric composition without changing the crystallography of the phase. Such compounds have been described in the case of the basic copper–zinc chromates.[6]

Ammonium, Sodium and Potassium Nickel Chromates.—Results similar to those obtained with the ammonium copper chromate were obtained with all experiments employing nickel. The precipitates were all crystalline and uniform in appearance, maroon in color, and insoluble in cold acids, but only approximated the desired chemical analysis, and showed variation in composition with varying precipitation conditions. The evidence again points to a solid-solution type of material similar to that postulated for the ammonium copper salt.

The sodium nickel chromate precipitate obtained in these experiments, which approximates the composition $Na_2O{\cdot}4NiO{\cdot}4CrO_3{\cdot}3H_2O$, except for about a 10% deficiency of nickel, is the first reported crystalline combination of sodium, nickel and hexavalent chromium.

Analytical Methods

Chromium present as Cr^{vi} was determined by potentiometric titration of the sulfuric acid solution of the salts with ferrous sulfate solution standardized against C.P. potassium dichromate.

Sodium was determined as the uranyl zinc triple acetate, according to the method of Barber and Kolthoff.[7] Cr^{vi} does not interfere; other heavy metals may theoretically replace zinc isomorphously in the triple acetate, but

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(6) J. B. Harry, R. H. Wellman, F. R. Whaley, H. W. Thurston, Jr., and W. A. Chandler, *Contrib. Boyce Thompson Inst.*, **15** [4], 195–210 (1948).

(7) H. H. Barber and I. M. Kolthoff, THIS JOURNAL, **50**, 1625 (1928).

are present in such small amounts, and differ so little in atomic weight, that their effect is negligible.

Ammonia was determined by distillation from the alkaline solution and absorption in standard sulfuric acid.

Zinc, cadmium and cobalt were determined by the anthranilate method of Funk and Ditt.[8] Cr^{vi} does not interfere provided the anthranilate is precipitated cold, and the *p*H is maintained as high as possible.

Nickel was determined gravimetrically as nickel dimethylglyoxime in the presence of tartrate to prevent precipitation of chromium.

Copper was determined iodometrically after reduction of Cr^{vi} to Cr^{iii} by concentrated hydrochloric acid or hydrogen peroxide in acid solution. It was found necessary to carry out the final titration with thiosulfate in mineral acid rather than acetic acid solution in order to prevent a fugitive end-point.

Water could not be directly determined on these compounds, as it could not be expelled without decomposing them. Consequently, indirect methods were employed where feasible. The salt was heated to a temperature above its decomposition point, where all water was removed. The extent of reduction of Cr^{vi} and evolution of oxygen was then determined and the weight loss corrected therefor. The water was then found by difference. Combustion methods would also be feasible, but the above method proved satisfactory. Water was not determined on the ammonium compounds, as even combustion methods are indirect in this case.

General Properties of the Compounds

The compounds described above are difficultly soluble in water, and dissolve incongruently. Repeated washing, especially with hot water, removes greater quantities of alkali metal and chromate ions, and the salts are eventually converted to a basic chromate, such as copper trioxychromate, $3CuO \cdot CrO_3 \cdot xH_2O$. Experiments on washing the finely divided sodium copper salt with cold water indicate that the extent of hydrolysis is not serious unless extremely large quantities of water are used

Ml. wash water/g. salt	CrO_3, %
Original material	47.5
520	46.1
1680	41.7

All compounds are readily soluble in cold dilute mineral acid, except the nickel salts, which must first be warmed. Heating at 175° does not remove the water from the compounds; water is only removed at higher temperatures, when decomposition occurs, with formation of a mixture of alkali chromate, heavy metal basic chromate, and heavy metal chromite, as evidenced by the formation of Cr^{iii} compounds. Decomposition of the ammonium compounds is even more profound. A reaction takes place at about 300° with feeble deflagration, evolution of nitrogen, water vapor, and ammonia and reduction of chromium to chromic oxide and intermediate oxides. The compounds are soluble in ammonium hydroxide solution, forming ammine ions of the heavy metals, but insoluble in organic solvents.

Discussion

The above data indicate that the series of double salts $M^{i}_{2}O \cdot 4M^{ii}O \cdot 4CrO_3 \cdot 3H_2O$, first described by Gröger,[1] is more extensive than at first supposed. Sodium may replace potassium and ammonium as the univalent element, and nickel forms crystalline materials approaching the typical composition.

In all cases, where a definite compound has been reported, its existence has been checked by several tests: (1) conformity to the theoretical analysis; (2) existence of crystals, which have been further checked for constancy of crystal angle wherever possible; (3) precipitation of the same product, confirmed both visually and by analysis throughout various stages of a batch precipitation (one precipitant) or under varying conditions of continuous precipitation (two precipitants).

The compounds obtained by Gröger[1] were obtained by precipitation of heavy metal salt by alkali chromate; under these conditions *p*H values during the precipitation range from 5 to 8, but it has been found in this laboratory that the potassium salts may be obtained at lower *p*H. In the present work, precipitation occurred at *p*H ranges of 2 to 5 for the most part. The inference to be derived from the data is that the potassium salts observed by Gröger have a wider range of stability than the sodium salts, all of which have been prepared at the lower *p*H range. In the precipitation of potassium zinc chromate, good crystals were prepared at *p*H 6.4.[3]

Variations are noted in the ability of the different metals to form these compounds. The formation of compounds apparently depends on the ionic radii involved. Although different values are given by different references,[9,10] the relative size of the transition ions appears to be $Ni < Cu < Co < Zn < Cd$, and of the alkali ions $Na < K < NH_4$. The large cadmium ion will not form compounds of this series with the small sodium ion, while the nickel ion forms materials approximating the type formula, with closest approach in the case of the sodium compound. The copper ion forms non-stoichiometric precipitates with ammonium ion. Additional compounds may be expected with rubidium and cesium and the larger transition ions, but these lie outside the scope of this paper.

In these compounds, the water is complexly held, possibly as hydroxyl groups, as shown by the fact that it is not removed by heating without completely decomposing the compound. Many possible structural arrangements can be suggested based on known coördination relationships, but final determination of the structure of these compounds must rest on X-ray data.

Similarity of crystal angles of the compounds, which form discrete crystals, and of empirical formulas, suggests the existence of an isomor-

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[8] H. Funk and M. Ditt, *Z. anal. Chem.*, **91**, 332-340 (1933).

[9] W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, N. Y., 1940.

[10] F. Ephraim, "Inorganic Chemistry," 4th ed., revised, tr. by P. C. L. Thorne and E. R. Roberts, Nordeman Publishing Co., New York, 1943.

phous series. This was further substantiated by the preparation of mixed sodium copper zinc salts by addition of sodium chromate solution to an equimolar mixture of zinc and copper trichromate solution until all zinc and copper were precipitated. The first crystals formed were a brownish maroon, indicating a predominance of the copper salt. As precipitation progressed, a continuous graduation in color to reddish-yellow was noted with no change in crystal form, a zinc-rich salt precipitating directly on the copper-rich crystals first formed. A typical product was uniform, brownish-red in color, composed mostly of aggregates of well-defined crystals of the general shape previously described. Single crystals showed a crystal angle of 62–63°. The crystals were identified as belonging to the general family of compounds by analysis for sodium and chromium: Found: Na_2O, 7.49; CrO_3, 47.52; molecular ratio, CrO_3: Na_2O = 3.94. Calculated (Cu salt): Na_2O, 7.43; CrO_3, 47.94; (Zn salt) Na_2O, 7.37; CrO_3, 47.55. Isomorphism evidently exists, but there is a considerable discrepancy in solubility of the two salts, the copper salt being the more insoluble at the lower *p*H.

An interesting development in the case of the ammonium double salts is the existence of a new series of compounds of the general formula $3NH_3\cdot 4M^{ii}O\cdot 4CrO_3\cdot 3H_2O$. The exact structure of these compounds is unknown, but a simple concept of their formation is the replacement of a water molecule in $(NH_4)_2O\cdot 4M^{ii}O\cdot 4CrO_3\cdot 3H_2O$ by NH_3. They appear to crystallize in hexagonal plates in those cases where discrete crystals have been observed.

Conclusion

1. The following new compounds have been prepared and described, members of the isomorphous series $M^{i}_{2}O\cdot 4M^{ii}O\cdot 4CrO_3\cdot 3H_2O$: $Na_2O\cdot 4CuO\cdot 4CrO_3\cdot 3H_2O$, $Na_2O\cdot 4CoO\cdot 4CrO_3\cdot 3H_2O$. They form characteristic tabular diamond-shaped crystals over a range of *p*H and concentration.

2. A new series of compounds, of the general formula $(NH_4)_2O\cdot 4M^{ii}O\cdot 4CrO_3\cdot NH_3\cdot 2H_2O$, or $3NH_3\cdot 4M^{ii}O\cdot 4CrO_3\cdot 3H_2O$, crystallizing in six-sided plates or aggregates, has been noted. The zinc and cobalt salts have been prepared and described.

3. Precipitates have been obtained approximating the above formulas in the case of ammonium copper chromate, ammonium nickel chromate, sodium nickel chromate, and potassium nickel chromate. These materials exhibit substantial variation in appearance and composition with varying precipitation conditions. They appear to be solid-solution type compounds with the property of forming definite crystals with an excess or deficiency of certain components of the lattice.

4. The series of compounds falls within a logical pattern, as determined by ionic ratios. The non-existence of the sodium cadmium chromate is in accord with this pattern, as are the non-stoichiometric compounds formed.

5. Preliminary data have been presented which may be helpful in the eventual determination of the structure of these compounds.

RESEARCH LABORATORIES
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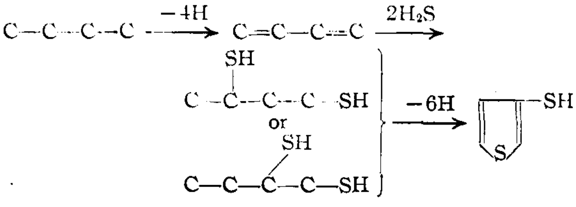
Derivatives of 3-Thiophenethiol

BY J. W. BROOKS, E. G. HOWARD[1] AND J. J. WEHRLE

The preparation of thiophene by the reaction of sulfur with *n*-butane at elevated temperatures has been reported by Rasmussen, Hansford and Sachanen.[2] These investigators obtained approximately one pound of so-called "tar" for every pound of thiophene produced. The tar has been investigated and found to contain 20–30% of 3-thiophenethiol. A possible mechanism for the formation of this compound is given.



In order to identify the thiol obtained from the tar as 3-thiophenethiol, the 2,4-dinitrophenyl sulfide derivative was prepared (m. p. 132.5–133°). The melting point corresponds to that of the 2,4-dinitrophenyl sulfide made from a sample of 3-thiophenethiol synthesized by Caesar and Branton.[3] Their synthesis involved the reaction of sulfur with the Grignard reagent prepared from 3-iodothiophene. The corresponding derivative of 2-thiophenethiol melts at 119°.[4]

3-Thiophenethiol is a colorless liquid possessing an offensive stench similar to that of benzenethiol.

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(1) Present address: Experimental Station, du Pont, Wilmington, Delaware.

(2) Rasmussen, Hansford and Sachanen, *Ind. Eng. Chem.*, **38**, 376 (1946).

(3) Unpublished work of P. D. Caesar and P. D. Branton of this Laboratory.

(4) Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).