NO_3^{2+} (36 hr.) both the isothiocyanato and nitro species are stable under the reaction conditions. In addition, when $Co(NH_3)_5N_3^{2+}$ is allowed to react under these conditions one finds 13.5% $Co(NH_3)_5NCS^{2+}$, in good agreement with Haim and Taube, so that it is apparent that the nitrite ion is not present in a large enough quantity to compete successfully with thiocyanate. Thus, the nitro complex must be formed from $Co(NH_3)_5H_2O^{3+}$.

The experiments reported here demonstrate conclusively that the aquation of $Co(NH_3)_5NO_3^{2+}$ does not proceed *via* the same intermediate which is formed when $Co(NH_3)_5N_3^{2+}$ is treated with nitrous acid, contrary to the assumptions of Haim and Taube. The virtually total formation of aquopentaammine as an intermediate and the independence of the rate of aquation on the presence of 0.50 *M* thiocyanate ion are in good agreement with the solvent-assisted dissociation mechanism proposed earlier.[2,8,8a]

Acknowledgments.—This work was supported by the U. S. Atomic Energy Commission, No. COO-1087-74. Professor F. Basolo suggested the nitrite ion reactions.

[8] T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961); R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964).

[8a] NOTE ADDED IN PROOF.—Repetition of the hydrolysis experiment in 0.5 *M* NaSCN with $[Co(NH_3)_5Br]Br_2$ gave the same result as for $[Cr(NH_3)_5NO_3](NO_3)_2$.

[9] NSF predoctoral fellow, 1961–1964.

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Transition Metal Acetylides

Sir:

The only well-characterized transition metal acetylides are those of yttrium and lanthanum, on the one hand, and of the copper and zinc group elements on the other, all of which form acetylides in at least one of their oxidation states. The only report on acetylides of other transition elements is Durand's claim that manganese, iron, cobalt, and nickel acetylides can be prepared by the reaction of calcium carbide with aqueous solutions of the respective metal salts.[1] Evidence for the proposed constitution of these compounds was based entirely on the evolution of acetylene on treatment with dilute hydrochloric acid, and no elemental analyses were recorded.

Terry[2] patented a method for recovering copper by the passage of acetylene through aqueous solutions of its salts, and the process was apparently also applicable to silver, mercury, nickel, osmium, and palladium. Since copper, silver, and mercury are known to form acetylides under such conditions, it seemed possible that the other elements might also be precipitated as acetylides, although this was not specifically claimed.

We have been unable to confirm the work of Durand with respect to the preparation of the acetylides of manganese, iron, cobalt, and nickel and conclude that his products were almost certainly unreacted calcium carbide, possibly coated with difficultly-soluble material. Moreover, all attempts to precipitate nickel, in any form, by the passage of acetylene through aqueous solutions of its salts have failed, although cuprous acetylide was produced when copper(I) solutions were so treated. Similar negative results were obtained from copper(II), manganese(II), iron(II), and cobalt(II) solutions.

Following Durand,[1] finely-ground calcium carbide (90% purity) was added to a solution of nickel chloride in water contained in a conical flask. The stopper was fitted quickly and the reaction allowed to proceed for 15 min. At the end of this time, the contents of the flask were filtered and the residue was washed repeatedly with 2 *M* acetic acid. Eventually, only a minute amount of material was left and this dissolved in 2 *M* hydrochloric acid, except for a trace of black material, probably free carbon, which floated on the solution. No nickel was detected in the hydrochloric acid solution.

In a more sophisticated experiment, a weighed amount of calcium carbide was added to a solution of known nickel content, in an evacuated system, and the evolved acetylene was quantitatively determined by its infrared spectrum. The volume of acetylene recovered was identical with that obtained by a straightforward water hydrolysis of calcium carbide. The small amount of residue after filtration was rinsed thoroughly with 2 *M* acetic acid, and the washings were added to the original filtrate. The filtrate and the residue were analyzed for nickel using both the dimethylglyoxime and pyridine–thiocyanate methods. No nickel was found in the residue, and this was confirmed by the excellent agreement between the values for the nickel content of the solutions before and after reaction. However, the residue was shown by qualitative analysis to contain calcium and it evolved a trace of acetylene when dissolved in 2 *M* hydrochloric acid. As before, a trace of free carbon was observed. In similar experiments with salts of manganese, iron, and cobalt, no transition elements were detected in the residues.

In a final series of experiments acetylene gas from a cylinder was passed through a trap at −80° to remove most of the acetone vapor and then successively through a flask containing a standard aqueous nickel(II) solution and a similar flask containing a copper(I) solution. After 24 hr. all the copper had been precipitated, presumably as the acetylide, but no precipitate was visible in the nickel solution. Repetition of the experiment with 2 *M* hydrochloric acid, 2 *M* sodium hydroxide, or aqueous ammonia in the nickel solution did not affect the result, though cuprous acetylide

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[1] J. F. Durand, *Compt. rend.*, **177**, 693 (1923).

[2] J. T. Terry, U. S. Patent 1,544,197 (June 30, 1925).

was always produced, at least to some extent, under all these conditions. Similar experiments with manganese, iron, and cobalt also gave negative results.

Conclusion.—The acetylides of manganese(II), iron(II), cobalt(II), and nickel(II) cannot be prepared under the conditions reported by Durand.[1] It is also unlikely that nickel can be recovered by the use of acetylene as suggested by Terry.[2]

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Book Reviews

Coordination Compounds. By DEAN F. MARTIN and BARBARA B. MARTIN. McGraw-Hill Book Co. Inc., 330 West 42nd St., New York, N. Y. 1964. x + 99 pp. 14 × 21 cm. Price, $1.95 paperbound, $4.95 clothbound.

The book is interesting and well written. The use of examples that make the subject seem alive and vital, as it reflects current research in inorganic chemistry, is especially good. Also, the inclusion of appropriate references so that the student can easily find more information is important for a book of this type. The authors have provided an excellent introduction to coordination chemistry.

The titles of the five chapters give a good indication of the range of topics covered: "The World of Coordination Compounds"; "The Years of Discovery"; "The Architecture of Coordination Compounds"; "The Years of Understanding"; and "Coordination Compounds in Solution." It seems to me that a fuller use of electronic configurations to describe ions of interest would have been useful since many beginning courses now cover this topic in some detail. I think that the only omission worth noting is the mention of ligand field theory without discussing in any detail one of its major successes, *i.e.*, explaining the colors of coordination compounds. The idea of ligand field theory is introduced in a clear and concise manner, and the explanation of the relationship between colors and field strengths would have completed this section on theoretical approaches to bonding very satisfactorily. It seems a shame to bring the student to this point and then stop before he "sees the light" or, in this case, "color."

The book is good factually. Almost anything that might be pointed out would be more in the nature of quibbling rather than a valid question or comment about what is written. I would guess that many students will not understand why both coordination number (CN) 4 for a planar arrangement and CN 6 can have radius ratios equal to between 0.41 and 0.59 and why the figure on p. 10 shows that CN 3 is better than CN 4. In fact, the sizes of the circles in the figure have a radius ratio equal to 0.39. The classic illustration that the arrangement of bonds around the Pt(II) ion is planar involving the resolution of the isobutylenediamine-*meso*-stilbenediamineplatinum(II) ion is sophisticated and satisfying, but many students will not appreciate this without the use of models. Of course this comment applies to the whole of stereochemistry and the authors have thoughtfully provided templates that will allow the student to construct models of the octahedron and tetrahedron.

"Coordination Compounds" can be recommended as a good introduction to the subject.

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Inorganic Polymer Chemistry. By F. G. R. GIMBLETT. Butterworth, Inc., 7235 Wisconsin Ave., Washington 14, D. C. 1963. ix + 452 pp. 15 × 25 cm. Price, $17.50.

Although the term "inorganic polymer" seems to have a different meaning to each person using it, Gimblett has not chosen to define it explicitly in his treatise. As "inorganic polymers" he covers, in more or less detail, everything from elements *per se* to coordination polymers containing organic bridging groups. In many instances "polymer" is used to include dimers, trimers, and other oligomers, and, indeed, a goodly portion of the book is devoted to such substances. The emphasis is on noncarbon-containing systems such as phosphates, silicates, phosphonitrilic halides, and binary inorganic compounds, with particular attention paid to the characterization of substances as polymers. There are only a few references to work published later than 1961.

Unfortunately much of the value of Gimblett's compilation is negated by careless writing. A sampling of statements that disturbed this reviewer follows:

"It is possible, as mentioned above, that the presence of excess phosphoric acid in the dehydration [sic] of $CdCO_3$, CdO, and various zinc compounds influences the nature of the final products.'"

"If sufficient KNH_2 is present, the second stage in the reaction may be visualized as: $[Co_2(NH_3)_8(NH_2)_2]^{4+} + NH_3$ [sic] $\rightleftarrows$ $[Co_2(NH_3)_7(NH_2)_3]^{3+} + NH_4^+$ [sic].

"The stability of these polynuclear amido complexes is strongly dependent upon the state [sic] of the solution."

"Another way of preparing alkoxides is to dissolve the metal hydroxide in the alcohol: $NaOH + EtOH \rightleftarrows NaOEt + H_2O$."

"Spontaneous formation of polymeric palladous chloride from the monomer [sic] is an example of addition polymerization."

"In the polyphosphoryl chloride system, again no ionization is possible and the chlorine atoms along the polymer chains are appreciably smaller than those [sic] existing in the phosphoryl dimethylamide system."

Mention should also be made of the references to bridging groups as bidentate ligands; to metal ions as cross-linking agents where they do not cross link; to $Mo_8O_{26}^{-4}$ as tetramolybdate; to a molecule existing as a number of resonance forms; to NH_3 in acid solutions, etc., and to inaccurately drawn formulas for metal phthalocyanines and an incorrect equation (3.146).

In concept this book is excellent, but it has not been prepared with enough attention to detail. In addition to the specific points listed, which are only representative of a number of items noted, there are inconsistencies in classification and awkwardness in arrangement that make the presentation unnecessarily hard to follow. The misprints noted should not lead to confusion.

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High-Temperature Materials, No. 1—Materials Index. By PETER T. B. SHAFFER. Plenum Press, 227 West 17th St., New York, N. Y. 1964. xx + 740 pp. 15.9 × 23.5 cm. Price, $17.50.

This book presents a data summary for properties of eight classes of high temperature materials: borides, carbides, mixed carbides, elements, nitrides, oxides, mixed oxides, and silicides