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Stabilities of Metal Derivatives of *o*-Substituted Azo Dyes

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The coordinating tendencies with metal ions of azo dyes which contain a hydroxyl, amino, or carboxyl group in one or more of the *ortho* positions have been studied in some detail. Such compounds have found many applications in the dying of fabrics (*1*) and in the preparation of organic pigments (*2*). Although numerous investigations have been carried out as to the light fastness, resistance to laundering, etc., of the metal compounds, almost no measurements have been made on the stability of these compounds toward dissociation into their constituent ions.

Formation constants of the metal derivatives (expressed as the general case)

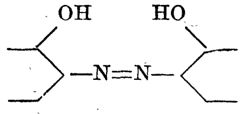
$$M\mathrm{Ch}_{n-1}^{m-(n-1)} + \mathrm{Ch}^- = M\mathrm{Ch}_n^{(m-n)},$$

(where M is the central metal ion, Ch^- is the chelate ion, m is the charge on the metal ion, and n is the number of Ch^- groups) have been measured using the Bjerrum (*3*) technique of potentiometric titration as modified by Calvin (*4*).

The decreasing order of stability of the divalent metal complexes with 4-(2-hydroxybenzeneazo)-3-methyl-1-phenyl-5-pyrazolone, a terdentate group, agrees with those already reported for monodentate and bidentate chelate groups (ammonia [*3, 5*], ethylenediamine [*5, 6*], salicylaldehyde [*5–8*], salicylaldehyde-5-sulfonic acid [*9*], β-diketones [*8, 10, 11*], tropolone [*12*], 8-hydroxyquinoline [*8*], 8-hydroxyquinoline-5-sulfonic acid [*13*], α-amino acids [*13, 14*], and alkyliminodiacetic acids [*15*] and is as follows: Cu > Ni > Co > Zn > Pb > Cd > Mn > Mg > Ca > Sr > Ba. The alkaline earths previously have not been included in such a series, although their noted order is the same as that found by Schwarzenbach (*16*) with iminodiacetic acid and other chelates of the same type.

The decreasing order of stability of the metal compounds of the triply charged metal ions with the aforementioned dye is as follows: Fe > Cr > Al, which is the same as that found by Cooperstein (*17*) with the acetylacetonates.

The relative order of coordination of the dyes with a given metal such as copper (II) is



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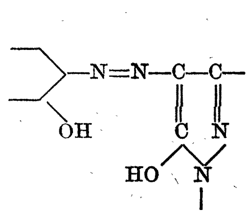

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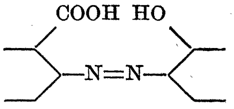

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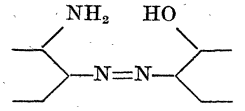

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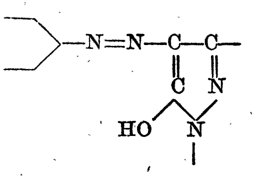

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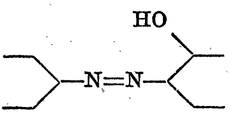

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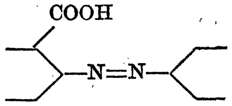

VII

As the above power of coordination with metal ions falls off, the number of metals which form compounds also decreases, so that the last member of the series

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forms a stable complex only with copper (II).

The regularities noted are as follows:

1. In a series of analogous dyes there is a decrease in stability of the metal compounds with increased acidity of the dye.
2. A terdentate group forms a more stable compound than a bidentate group.
3. The hydroxyl group is a stronger coordinating group than the carboxyl group.
4. The simple pyrazolone dyes (Type V), although stronger acids than the simple monohydroxy (Type VI) compounds, form more stable compounds.

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Comments and Communications

Alternaria within Pericarp of Wheat Seed

In a communication to *Nature* (*1*) on "The problem of wheat rust," I stated that I obtained *Alternaria* from a majority of fresh and healthy Indian wheat seeds of the current year when they were aseptically treated and planted in culture tubes. From culture of surface-sterilized grains of Barsée wheat (a rust-resistant variety), Miss Hyde (June 1950) observed that the "most common subepidermal fungus is *Alternaria tenuis* (in 64.4% of grains);" she further holds that the subepidermal mycelium apparently arises either from systemic infection of the wheat plant (as in case of *Lolium* spp.) or from fungal spores and hyphae present on the outside of the developing grains and among the dead floral parts. She has not been able as yet, however, to find an instance of actual penetration of the epidermis—the method of entry of the subepidermal mycelium—although she is still trying to find it. From the basal internode (about 1–2 in. long) of flowering stems of Barsée wheat and from stems immediately below the inflorescence, she could get, under aseptic condition in culture plates, *Alternaria tenuis* in 40 and 43 stems out of 70 (*cf.* Table 3, at p. 355, *loc cit.*).

When healthy wheat seeds, aseptically treated, germinated within the culture tubes, sections of the plumules and radicles of healthy wheat seedlings showed the same septate and branched hyphae within their tissues, which in pure culture produced *Alternaria* spores; and, as stated in *Nature*, "repeated isolation of mycelium of *Alternaria sp.* from surface-sterilized seeds indicated that the fungus remained within the seed tissues." Christensen (*3*) seems to hold *Alternaria* mostly to be a storage mold in the case of high-grade wheats. But it is clear (*4*) that he definitely holds *Alternaria* to be "of no known significance in the deterioration of stored seed." Now, of the two alternatives left (i.e., parasite and symbiont), *Alternaria* obviously cannot be a parasite within the seed pericarp of all the healthy wheat plants of the world. Hence, I hold that there can be no other conclusion than that *Alternaria* should be regarded as a symbiont and that further work on eradication of wheat rust should proceed along this new line.

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Zoological Nomenclature

Notice is hereby given that, as from April 15, 1953, the International Commission on Zoological Nomenclature will start to vote on the following cases in the Class Aves, involving the possible use of its plenary powers for the purposes specified in brackets against each entry. Full particulars of these cases were published on October 15, 1952, in the *Bulletin of Zoological Nomenclature*, in Triple-Part 1/3 of Vol. 9.

(1) *Colymbus* Linnaeus, 1758, and *Gavia* (all uses prior to *Gavia* Forster, 1788) [suppression]; (2) *caspicus* Hablizl, 1783, *Colymbus* [suppression]; (3) *cafra* (*Otis*), *cafer* (*Cuculus*), *sulphuratus* (*Cuculus*), *flavescens* (*Lanius*), all of Lichtenstein, 1793 [suppression]; (4) *nortoniensis* Gmelin, 1789, *Fringilla* [suppression]; (5) *natka* (*Lanius*) and *septentrionalis* (*Lanius*), both of Gmelin, 1788, and *eimeensis* (*Columba*), *unalaschkensis* (*Hirundo*), *borealis*