

conditions cause the release of a certain amount of aluminum from the silicate lattice which apparently stays on the exchange surface and is released through exchange reactions.⁹ It is found in the filtrate of those soils which are acid enough to prevent its precipitation. In soil studies it is usually measured as part of the acidity of the solution where phenolphthalein is used as an indicator. Therefore, although the equations should permit one to calculate the pH or H-ion concentration of the supernatant solution in equilibrium studies, the pH will usually be found to be higher than calculated since part of the release calculated as hydrogen is present as aluminum.

It would be difficult to evaluate the probable use of the above equations in studies concerned with such problems as the investigation of exchange diffusion as postulated by Winters¹⁰ or the special case of exchange diffusion called contact exchange by Jenny.¹¹ While it is theoretically possible to consider such a process as occurring in the absence of electrolytes, under soil conditions it becomes impossible to consider it separately from the processes involved in the reactions covered by the above equations because both exchangeable ions and electrolytes occur in the micellar water.

Either a direct exchange (contact exchange) or an indirect exchange (exchange through medium of an electrolyte) must be supported by a continuous renewal of the ions at the contacting

(9) H. Paver and C. E. Marshall, *J. Soc. Chem. Ind.*, **53**, 750 (1934).

(10) Eric Winters, Doctor's Thesis, University of Illinois, 1938.

(11) H. Jenny and R. Overstreet, *Soil Sci.*, **47**, 257-272 (1938).

surfaces, a renewal which must come as a result of exchange diffusion or of diffusion as an electrolyte or, as is probable in the soil, of a combination of both processes. Without this renewal "contact exchange" could supply very few ions to the plant roots which contact only a very small part of the colloid surfaces in the soil.

Summary

The immediate equilibria between mixtures of exchangeable cations as they occur naturally in clays and small amounts of an added cation have been studied.

Cation-exchange equations have been developed from the data obtained which enable calculation of the release (or adsorption) of an individual cation in the presence of one or more complementary cations on the colloid when one or more cations are added as highly ionized electrolytes.

The relative "ease of release" for univalent and bivalent exchangeable cations is in the order $Na > K > Mg > Ca > H$ as shown by their f values in the above-mentioned equations.

The exchangeable bases as usually determined by leaching with a neutral salt solution are shown to be those which are in equilibrium with added electrolytes after a short shaking period and are defined as readily exchangeable bases.

The secondary effect of the aluminum of the silicate lattice on the pH of the supernatant solution in acid clay studies is discussed in relation to the application of base-exchange equations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF POMONA COLLEGE]

The Configuration of Complex Kojates Formed with Some Transition Elements as Determined by Magnetic Susceptibility Measurements

BY JACK W. WILEY, GEORGE N. TYSON, JR., AND JACK S. STELLER

Organo-metallic compounds have been widely investigated in recent years.¹ In this work it has been found possible to synthesize complex kojates containing the divalent form of the transition elements manganese, iron, cobalt, nickel and copper, in the quadricovalent state, with kojic acid. The magnetic susceptibilities of these complexes have been measured and, on the basis of these results, the most probable configurations

have been assigned to the molecules. Kojic acid readily forms complexes with divalent ions other than those reported in this work, such as zinc and cadmium.

Experimental

Synthesis.—Sugar free kojic acid (2-hydroxymethyl-5-hydroxy- γ -pyrone) was neutralized with sodium hydroxide and adjusted to a pH of approximately 9. J. T. Baker and Co. c. p. metal acetate salts were used as the source of the metal ion, except the ferrous ion was obtained from

(1) Baudisch and Welo, *Chem. Rev.*, **15**, 1 (1924).

ferrous ammonium sulfate. The cupric complex of kojic acid was synthesized using the identical method of Barham and Smits.² The complex kojates of nickelous, cobaltous, ferrous, and manganous ions were synthesized by much the same procedure, except that a 10% excess of the metal ion was used instead of the 35% excess used for the copper complex formation. In addition, the volume of solution from which the cobaltous and nickelous kojates were precipitated was about one-fourth, and the ferrous and manganous kojates were precipitated from a volume of one-tenth that used for the copper kojate. The cobaltous and nickelous kojates precipitated slowly as compared with the other compounds, and required several days for relatively complete precipitation.

The precipitates were filtered, thoroughly washed, and dried at 90° for over six hours, after which the compounds were finely powdered and analyzed.

The yield for the cupric complex is quantitative.² The approximate yields obtained for the other complexes are shown in Table I. The metal analyses, run by standard macro procedures, are given also in Table I, together with the colors of the various complexes.

TABLE I

Complex kojate of	Metal, %		Color	Approx. yield, %
	Calcd. ^a	Found		
Cu · 1/2H ₂ O	17.92	18.07	Green	99.0
Ni · 1/2H ₂ O	16.78	16.97	Green	96.7
Co · 1/2H ₂ O	16.83	16.68	Yellow	79.0
Fe	16.53	16.40	Red	92.9
Mn	16.29	16.33	Yellow	94.4

^a The most likely amounts of water of crystallization are 1/2H₂O in the cases of the first three complexes, as shown by the metal analyses, and the data of Barham and Smits in the case of the cupric complex.² The ferrous and manganous complexes evidently do not contain water.

Magnetic Measurements.—The results of the magnetic measurements on the solid crystals made by the Gouy method at 22° are shown in Table II. In the column listing the Bohr magnetons, the calculations have been made assuming complete quenching of the orbital moment. In the conversion of the experimental data into Bohr magnetons, a correction has been made for the diamagnetism of the molecule.

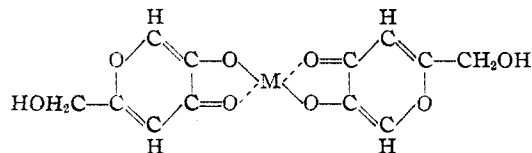
TABLE II

Complex kojate of	$\bar{X}_s \times 10^6$	$\bar{X}_m \times 10^6$	Bohr magnetons		Unpaired electrons present
			Exptl.	Calcd.	
Cu	4.10	1466	1.9	1.73	1
Ni	12.23	4166	3.2	2.83	2
Co	27.97	9539	4.8	3.88	3
Fe	35.81	12100	5.4	4.90	4
Mn	47.22	15910	6.2	5.92	5

(2) Barham and Smits, *Ind. Eng. Chem., Anal. Ed.*, **11**, 31 (1939).

Discussion

The formula assigned to kojic acid has been fully discussed elsewhere.³ Using the accepted formula, the structures of the metal complexes can be written as



(M represents any of the five divalent metal ions)

As seen from Table II, the magnetic data show that the divalent complexes of nickel, cobalt, iron and manganese are tetrahedral and ionic. However, in the case of the cupric complex, the magnetic evidence does not indicate whether the compound is planar or tetrahedral, as both forms would exhibit one unpaired electron.

The use of the ferric complex of kojic acid for the quantitative estimation of iron has been recently reported.⁴ Conditions for the use of kojic acid for the determination of ferrous ion in the presence of ferric ion are being currently investigated. In addition, the complexes of ascorbic acid with transition element ions and the configurations of the oxygenated and hydrogenated compounds will be reported in the near future.

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Summary

Complex kojates of divalent copper, nickel, cobalt, iron, and manganese have been prepared (the synthesis and analysis of which have been given), and the magnetic susceptibilities determined. On the basis of these results, it has been found that the configuration of the copper complex is either tetrahedral or planar, while the divalent nickel, cobalt, iron, and manganese complexes are tetrahedral.

CLAREMONT, CALIF.

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(3) Barham and Smits, *Trans. Kansas Acad. Sci.*, **37**, 91 (1934).

(4) Moss and Melton, *Ind. Eng. Chem., Anal. Ed.*, **13**, 612 (1941).