single curve is obtained when $y = Z/5$ is plotted as a function of $X = \log T_D - 5 \log [H^+]$ (Figure 9). The complexes formed in appreciable amounts in solution can therefore be written in the form $(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_n{}^{-7n-2}$.

In view of the fixed stoichiometry (1:1) of the uranyl citrate system under investigation and on the basis of the fact that a definite inflection of the titration curve occurs at $4^2/_3$ moles of base per mole of uranyl chelate, the value of n in the "core plus links" formula should be equal to 2. Thus, the polynuclear species present in the buffer region of the titration curve between 3 and $4^2/_3$ moles of base per mole of uranyl chelate appears to be predominantly hexameric and has the formula $(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_2{}^{16-}$ (structure IV, Chart I). The hexameric chelate may be formed either directly or through the formation of a tetranuclear chelate intermediate (structure III, Chart I). By applying the method of calculation reported by Sillén and Hietanen[15] and Hietanen,[16] the equilibrium constant (K_2) for the formation of the hexanuclear chelate was determined.

$$K_2 = \frac{[(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_2{}^{16-}][H^+]^{10}}{[(UO_2)_2L_2{}^{2-}]^3} = 10^{-47.9}$$

A consideration of the results of the uranyl citrate, uranyl malate, and uranyl tartrate[5] systems brings out a striking similarity, *viz.*, in each of these systems the complex species formed in solution in the buffer range (pH 2–4) is predominantly binuclear. Above pH 4, each of these binuclear chelates reacts with hydroxide ions and polymerizes further. The dimerization constants (K_d) follow the order citrate > malate > tartrate. However, the differences in stability constants do not exceed 0.6 log K unit. Consideration of the nature of the equilibria involved in the formation of these binuclear chelates and a comparison of the dimerization constant (K_d) would strongly suggest the involvement of the α-hydroxyl group of the ligands in bridging. In the light of this observation it is of interest to reconsider the data thus far reported on the polynuclear uranyl complexes. The hydrolysis of the uranyl–Tiron chelate (pyrocatechol-3,5-disodium sulfonate) and formation of a ternuclear species at pH 5 has been reported by Gustafson, *et al.*[17] They have visualized a possible structure for the polynuclear uranyl complex which involves both the hydroxo groups and the ligand groups containing oxygen donors in the bridging of the uranyl ions. Richard, *et al.*,[18] have reported the formation of a binuclear uranyl chelate with 8-quinolinol-5-sulfonate which would presumably involve the phenoxide ion of the ligand in the bridging. In the polymerization of the uranyl–HIMDA chelate[4] (N-hydroxyethyliminodiacetic acid), it could be suggested that the bridging between the uranyl ions may take place through the alkoxide group of the ligand. It should thus be noted that all the polynuclear uranyl complexes thus far reported have ligands with hydroxyalkyl or phenolic groups. Of course, the reverse is not true; many ligands with these functional groups do not form polynuclear uranyl complexes. This interesting observation leaves open a fundamental question for future investigations, *viz.*, how fundamental or how essential are hydroxyorganic groups in the polymerization reactions of uranyl complexes?

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Complexes Derived from Strong Field Ligands. XIX. Magnetic Properties of Transition Metal Derivatives of 4,4′,4″,4‴-Tetrasulfophthalocyanine

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Received October 12, 1964

The tetrasulfophthalocyanine complexes of manganese, iron, cobalt, nickel, and copper have been prepared in high purity and the magnetic moments of these substances have been determined both in the solid state and in solution. Solid state determinations are complicated by cooperative interactions. The iron(II) complex is a reversible oxygen carrier in the solid state. In aqueous solution, Mn(II), Co(II), Ni(II), and Fe(III) are spin paired. The ligand field strength of tetrasulfophthalocyanine is comparable to that of cyanide ion.

Introduction

Although a number of investigations[1–5] have been devoted to the magnetic properties of unsubstituted metal phthalocyanines, magnetic susceptibilities have

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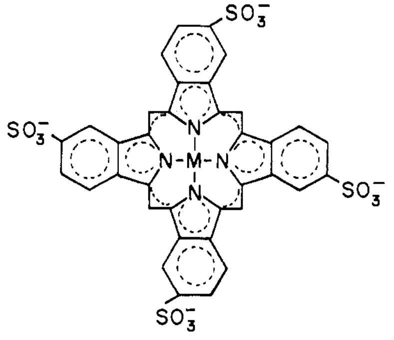
not previously been measured for their water soluble, tetrasulfo derivatives (structure I).



I

Experimental

Materials.—The monosodium salt of 4-sulfophthalic acid was obtained from the Aldrich Chemical Co. and used without further purification. All other chemicals were of reagent grade.

Magnetic Measurements.—Magnetic moments were obtained at room temperature by the Gouy method, using mercury(II) tetrathiocyanatocobaltate(II) and demineralized, doubly-distilled water as standards. Each value reported is an average of at least two, and more often five, independent determinations. The values are generally reproducible to ±0.05 B.M. for 0.025 *M* solution and to ±0.10 B.M. for the solids, with the average deviation in no case exceeding ±0.15 B.M. This greatest deviation occurs with solid samples at the lowest magnetic field strength. The results of a magnetic anisotropic study[6] and Pascal's constants[7] were used to calculate the diamagnetism of metal-free tetrasulfophthalocyanine. These corrections are -550, -543, and -569×10^{-6} for the tetrasodium salt, the trisodium salt, and the oxygen-containing monosodium salt, respectively.

Analyses.—Microanalyses were performed by Schwarzkopf Microanalytical Laboratories and by Gabraith Microanalytical Laboratories.

Tetrasodium Salt of Cobalt(II) 4,4′,4′′,4′′′-Tetrasulfophthalocyanine 2-Hydrate.—The procedure is adapted from the methods of Baumann[8] and Fukada.[9] The monosodium salt of 4-sulfophthalic acid (43.2 g., 0.162 mole), ammonium chloride (4.7 g., 0.09 mole), urea (58 g., 0.97 mole), ammonium molybdate (0.68 g., 0.0006 mole), and cobalt(II) sulfate 7-hydrate (13.6 g., 0.048 mole) were ground together until homogeneous. Nitrobenzene (40 ml.) was added to a 500-ml. three-necked flask fitted with a thermometer, a condenser, and a cork. The nitrobenzene was heated to 180°. The solid mixture was added slowly, with stirring, while keeping the temperature between 160 and 190°. The heterogeneous mixture was heated for 6 hr. at 180°. The crude product, a solid cake, was ground and washed with methanol until the odor of nitrobenzene could no longer be detected. The remaining solid was added to 1100 ml. of 1 *N* hydrochloric acid saturated with sodium chloride. This step is crucial for the removal of excess cobalt(II) from the product. The solution and accompanying undissolved material were briefly heated to boiling, cooled to room temperature, and filtered. The resulting solid was dissolved in 700 ml. of 0.1 *N* sodium hydroxide. The solution was heated to 80° and insoluble impurities were immediately separated by filtration. Sodium chloride (270 g.) was added to the solution. At this point some of the solid product precipitated. The slurry was heated and stirred at 80° until ammonia evolution stopped. The product was obtained by filtration and the initial reprecipitation process was repeated two additional times. The solid was separated and washed with 80% aqueous ethanol until the filtrate was chloride-free. This product was refluxed for 4 hr. in 200 ml. of absolute ethanol. The blue, pure product was filtered and dried overnight *in vacuo* over P_2O_5; yield 80%.

Anal. Calcd. for $C_{32}H_{12}NiO_{12}S_4Na_4Co \cdot 2H_2O$: C, 37.82; H, 1.59; N, 11.03; S, 12.62; Co, 5.80. Found: C, 38.01; H, 1.80; N, 11.09; S, 12.55; Co, 5.68, 5.75.

4,4′,4′′,4′′′-Tetrasulfophthalocyanine Derivatives of Other Metals.—Complexes containing nickel(II), copper(II), manganese(II), and an oxygen adduct of iron(III) have been prepared by procedures similar to that detailed for cobalt(II) above. These procedures are also adapted from those of Baumann[8] and Fukada.[10–14]

Anal. Calcd. for $C_{32}H_{12}N_8O_{12}S_4Na_4Ni$: C, 39.24; H, 1.24; N, 11.44; S, 13.09; Ni, 5.99. Found: C, 39.52; H, 1.66; N, 11.38; S, 13.51; Ni, 5.84, 5.74. Yield 90%.

Anal. Calcd. for $C_{32}H_{12}N_8O_{12}S_4Na_4Cu \cdot 2H_2O$: C, 37.66; H, 1.58; N, 10.98; S, 12.56. Found: C, 37.55; H, 2.01; N, 10.71; S, 12.47. Yield 55%.

Anal. Calcd. for $C_{32}H_{13}N_8O_{12}S_4Na_3Mn \cdot 2H_2O$: C, 38.83; H, 1.73; N, 11.32; S, 12.95. Found: C, 38.86; H, 1.72; N, 11.61; S, 12.47.

Anal. Calcd. for $C_{32}H_{15}N_8O_{14}S_4NaFe \cdot 3H_2O$: C, 38.56; H, 2.12; N, 11.24; S, 12.87; Fe, 5.60. Found: C, 38.10; H, 1.95; N, 11.22; S, 12.84; Fe, 5.32, 5.40. Yield 40%.

Results and Discussion

Highly purified samples of the tetrasulfophthalocyanines have been prepared by modifications of the procedures reported by Fukada[9–14] and Baumann.[8] The original methods yield products containing variable, but significant amounts of uncomplexed metal ion as persistent impurities. Because of this, the very high formula weights, and other difficulties, elemental analyses do not provide adequate assurance of purity. It is especially true for the nickel(II) and cobalt(II) complexes that the susceptibility measurement provides a more sensitive criterion of purity.

The magnetic susceptibilities and moments of the tetrasulfophthalocyanine complexes of manganese, iron, cobalt, nickel, and copper have been determined in both aqueous solution and in the solid state. The results are summarized in Tables I and II. The expected fully spin-paired ground state is observed for the nickel(II) complex. In the solid state (Table I), Mn(II), Co(II), and Cu(II) all exhibit magnetic moment values that vary with field strength, indicating intermolecular interactions. Havemann, Haberditzl, and Mader[3] report that the magnetic moments of the unsubstituted phthalocyanines of Co(II) and Fe(II) are field dependent. In these earlier studies the materials were much more difficult to purify so that the possibility of the presence of ferromagnetic impurities could not be eliminated. The limited data presented in Table I, when extrapolated to infinite magnetic field, yield values of μ_{eff} compatible with those observed for solutions of the Co(II), Mn(II), and Cu(II) compounds.

In the solid state the magnetic behavior of iron tetrasulfophthalocyanine is more complex. The product prepared from hydrated iron(II) sulfate reacts

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TABLE I

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF METAL TETRASULFOPHTHALOCYANINES (MSPc) IN THE SOLID STATE[a]

Compound	Field strength, kgauss	(complex) $\chi_M \times 10^6$	μ_{eff}, B.M.
$Co^{II}SPc$	7.8	+1225	2.07
	6.4	+1449	2.20
	3.2	+1763	2.36
FeSPc[b]	7.8	+3369	3.08
FeSPc[c]	7.8	+8986	4.80
$Mn^{II}SPc$	7.8	+2972	2.94
	6.4	+3516	3.17
	3.2	+5653	3.90
$Cu^{II}SPc$	7.8	+1449	2.21
	6.4	+1903	2.44
	3.2	+2737	2.83
$Ni^{II}SPc$	7.8	−358	...

[a] At room temperature. [b] In the presence of dry air after drying 24 hr. at 100° *in vacuo*. [c] In the presence of dry, oxygen-free nitrogen after drying 24 hr. at 100° *in vacuo*.

reversibly with molecular oxygen. When rigorously dried in the absence of oxygen, the moment approaches a maximum value of 4.80 (±0.08) B.M., while equilibration with dry air produces a value of 3.08 (±0.10) B.M. After some 30 to 40 absorption cycles, the activity is diminished. Although the probable existence of cooperative effects invalidate such a conclusion, the oxygen-free system approached the spin-only value for high-spin iron(II).

From the magnetic moments determined for 0.025 *M* aqueous solutions of the tetrasulfophthalocyanines (Table II) it may be concluded that the cobalt(II), iron(III), manganese(II), and nickel(II) complexes are spin-paired. The solution magnetic moment value of 1.80 B.M. in the case of the iron compound indicates one unpaired electron and, presumably, that the iron is present in the trivalent state. This result clarifies an earlier discrepancy[15,16] and demonstrates that the species in aqueous solutions that have not been protected from air is an iron(III) complex. The fact that the complexes of cobalt(II), nickel(II), iron(III), and manganese(II) are all spin-paired in aqueous solution attests to the great ligand field strength of tetrasulfophthalocyanine. Spin-paired complexes of manganese(II) are very rare. Only such extreme ligands as cyanides[17] and isonitriles[18] have previously been reported to produce spin-paired Mn(II). Thus, the phthalocyanine ring appears to exhibit a ligand field strength approaching that of cyanide.[19]

TABLE II

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF METAL TETRASULFOPHTHALOCYANINES (MSPc) IN SOLUTION[a]

Compound	$\chi_M \times 10^6$	μ_{eff}, B.M.
$Co^{II}SPC$	+940	1.88
$Fe^{III}SPc$	+824	1.80
$Mn^{II}SPc$[b]	+1050	1.94
$Cu^{II}SPc$	+768	1.77
$Ni^{II}SPc$	−441	...

[a] 0.025 *M* aqueous solutions at 20° and 19 kgauss. [b] Same μ_{eff} at 19 and 12 kgauss.

The spin-paired magnetic moment values found in solution fortify the conclusion, derived from the solid state measurements of cobalt(II), copper(II), and manganese(II) complexes, that cooperative effects exist in the solid state. In contrast, the results of the solution measurements are most easily interpreted and lead to the conclusion that the cooperative effects are greatly lessened, if not completely eliminated, in 0.025 *M* aqueous solution. Although the consideration of cooperative effects in solution might appear, after cursory thought, to be baseless, it must be recognized that the reported tendency of metal tetrasulfophthalocyanines to dimerize[15,20] could yield some such effect. The phenomena attributed to dimer formation are of a nature that might have implied micelle formation rather than true solution. Domain effects in the micelles might produce a field dependence under circumstances of this sort. The fact that a solution value of 1.94 B.M. was observed at both 19 and 12 kgauss for the manganese(II) complex (which has the strongest field dependence in the solid state) supports the conclusion that cooperative effects are eliminated by true dissolution in aqueous media.

To the extent that the analogy applies between the phthalocyanine ligands and the porphyrins occurring in nature, it may be concluded that these extremely versatile natural catalysts involve in-plane fourfold coordination approaching the extreme high limit of ligand field strengths.

Acknowledgment.—These investigations have been made possible by an unrestricted grant from the Research Corporation.

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