[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

The Magnetic Susceptibilities of Some Complex Cyanides with Transition Element Cations

BY JOHN RICHARDSON AND NORMAN ELLIOTT

The crystal structures of "soluble" and "insoluble" prussian blue have been reported by Keggin and Miles.[1] Information about the nature of these substances has been extended by van Bever[2] who has investigated the structures of the ferricyanides of Cd^{++}, Mn^{++}, Zn^{++}, Co^{++}, Cu^{++} and Ni^{++}.

All of the compounds so far studied have the cubic structure shown in Fig. 1. Each heavy metal atom is surrounded by either six nitrogen or carbon atoms at the corners of a regular octahedron. Alkali or other heavy metal ions, not shown in the figure, occupy equivalent positions at the centers of the small cubes.

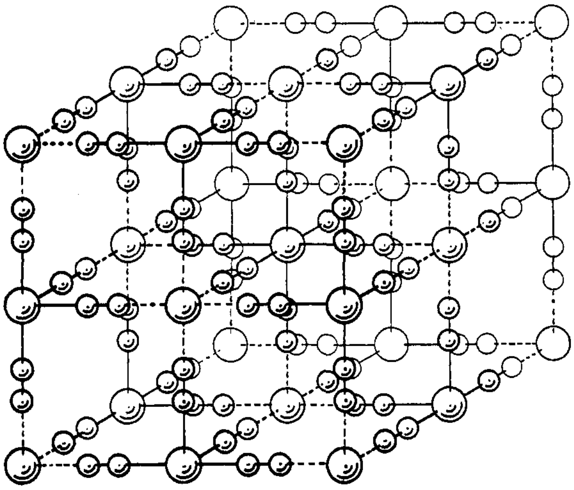

Fig. 1.

The nature of the chemical bonds between the cyanide and the heavy metal ions has been discussed by Welo and Davidson,[3] who measured the magnetic susceptibilities of "soluble" and "insoluble" prussian blue, and by Davidson,[4] who studied the rate of formation of prussian blue from solution.

Whether the chemical bonds in these compounds are ionic or covalent, or a combination of the two forms, has not been decided from the investigations so far, although the evidence suggests that one ion is a complex cyanide and the other is a simple metal ion.[5]

We have made several of these insoluble complex cyanides and have measured their magnetic susceptibilities. The compounds $K_2MnFe(CN)_6$, $K_2CoFe(CN)_6$, $K_2CuFe(CN)_6$, $KNiCo(CN)_6$, $KCoCo(CN)_6$, and $KCoCo(CN)_6 \cdot 2H_2O$ were prepared by adding 1 *f* solutions of the appropriate sulfates or nitrates to twice the volume of 1 *f* $K_4Fe(CN)_6$ or $K_3Co(CN)_6$ solutions. The suspensions obtained were dialyzed until excess anions were shown to have been removed. The salts were then evaporated to dryness and finally dried to constant weight at 100°; $KCoCo(CN)_6 \cdot 2H_2O$, which loses its water of crystallization at 100°, was dried at 60°. Each salt was analyzed for the heavy metals present. Duplicate analyses agreed with each other and with the percentages based on the above formulas to within a few tenths of a per cent.

Susceptibility measurements were made on the solid compounds by the Gouy method. Measurements were made at 20° only. It was found that results could be duplicated to within 1%. The magnetic moments in Bohr units were calculated with the formula

$= 2.84\sqrt{(\chi_m + 100)T}$, where μ = magnetic moment, χ_m = molar susceptibility, T = degrees absolute, 100 = diamagnetic correction.

The results are shown in Table I.

TABLE I

Compound	μ, exptl.	$\mu, \sqrt{4s(s+1)}$	$\mu, \sqrt{l(l+1)+4s(s+1)}$	μ, obsd. range
$K_2MnFe(CN)_6$	6.05	5.92	5.92	5.9
$K_2CoFe(CN)_6$	4.90	3.87	5.20	5.0–5.2
$K_2CuFe(CN)_6$	1.85	1.73	3.00	1.9–2.0
$KCoCo(CN)_6$	5.30	3.87	5.20	5.0–5.2
$KCoCo(CN)_6 \cdot 2H_2O$	5.30	3.87	5.20	5.0–5.2
$KNiCo(CN)_6$	3.10	2.83	4.47	3.2

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(1) J. F. Keggin and F. D. Miles, *Nature*, **137**, 577 (1936).

(2) A. K. van Bever, *Rec. trav. chim.*, **57**, 1259 (1938).

(3) D. Davidson and L. A. Welo, *J. Phys. Chem.*, **32**, 1191 (1928).

(4) D. Davidson, *J. Chem. Education*, **14**, 238 (1937).

(5) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

The observed moments agree with those calculated on the assumption that each substance contains a ferro- or cobalticyanide ion in which the transition element is forming d^2sp^3 bonds[6] to the cyanides; the other heavy metals exist as simple ions. The experimental values are also in accord with previous observations of the magnetic moments of these ions; manganese, nickel, and copper have very little orbital moment, while that of cobalt is nearly unquenched.[7] The magnetic moments calculated on the basis of any other structural formulas than the one suggested here are incompatible with the experiments. Calculations were made for each compound using the four structural formulas that would permit all possible combinations of ionic and d^2sp^3 bonds. Allowance was made for the moments arising from spin alone and also for maximum orbital contribution.

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Summary

The compounds $K_2MnFe(CN)_6$, $K_2CoFe(CN)_6$, $K_2CuFe(CN)_6$, $KCoCo(CN)_6$, $KCoCo(CN)_6 \cdot 2H_2O$ and $KNiCo(CN)_6$ have been prepared and their magnetic susceptibilities measured. The results are in agreement with the assumption that covalently bonded ferrocyanide or cobalticyanide ions are present in the compounds containing ferrous or cobaltic ions, respectively. All other heavy metals are present as simple ions.

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[6] Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[7] See J. H. van Vleck's discussion, "The Theory of Electric and Magnetic Susceptibilities," Oxford at the Clarendon Press.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The System Ethyl Alcohol–Glycerol–Benzene at 25°

BY HUGH J. McDONALD

A review of the literature showed that no data had been collected on the solubility relationships of the system, ethyl alcohol–glycerol–benzene. The distillation of such a ternary solution, with the determination of liquid–vapor composition data, should be interesting. There has been evident, also, during the last few years, considerable interest in the problem of the separation of the pure components from mixtures of glycerol and ethyl alcohol but very little work has been done on the effect of a third component on their mutual solubility. As a preliminary step in the study of the system, it was thought advisable to determine the region of immiscibility and the tie line relationships.

Materials.—Thiophene-free benzene, the best grade obtainable from Eastman Kodak Company, was used without further purification.

Ethyl alcohol (95%) was kept for a week in contact with dried calcium oxide and shaken from time to time, then distilled. The process was repeated, when the alcohol distilled, using a long fractionating column, within three-tenths of a degree; the middle portion was used.

Glycerol of C. P. grade was purified by repeated distillation under reduced pressure.

Procedure and Results.—The titrations involved in determining the curve bounding the region of immiscibility were carried out at 25.00 ± 0.05° in small glass-stoppered bottles, which were shaken in the constant temperature bath. Preliminary titrations were made and the curve sketched in, so that in the final titrations dropwise addition of alcohol was required over only a small range.

The end-points, it was found, were most accurately determined by adding the ethyl alcohol to the benzene–glycerol mixture until the cloudiness just disappeared, rather than trying to observe the first appearance of cloudiness on adding benzene to the ethyl alcohol–glycerol mixtures. The disappearance of cloudiness was observed by looking through the solution at a light bulb behind the all-glass water-bath.

It had been hoped that measurements of the refractive indices along the immiscibility curve would serve to determine the distribution of ethyl alcohol between glycerol and benzene. It was found, however, that the refractive indices changed only a little in the third decimal place all along the top of the curve. Surface-tension measure-