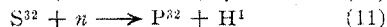
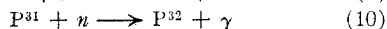
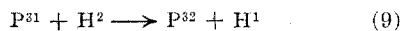


In other experiments it has been possible to establish the presence of extremely small amounts of phosphorus and sulfur as a result of the appearance of the 14-day electron emitting activity of P^{32} . The P^{32} was formed according to the reactions



For example, a neutron bombardment of a sheet of paper revealed the presence of the sulfur as the result of reaction (11).

This research has been made possible through the generous cooperation of the Research Corporation, the Chemical Foundation and the Josiah Macy, Jr., Foundation.

Summary

It is shown how it is possible to detect and identify very small amounts of impurities by means of their characteristic half-lives, after the substance containing the impurities has been rendered radioactive by bombardment with charged particles of high energy or with neutrons. With the help of a chemical separation after the bombardment, impurities present to the order of one part in a million can sometimes be detected. For example, a gallium impurity of six parts per million was found in a sample of iron. Impurities to the extent of one part in one thousand to ten thousand can often be detected without subjecting the sample to chemical analysis.

BERKELEY, CALIFORNIA

RECEIVED MAY 16, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 642]

The Magnetic Properties and Structure of Manganous and Cobaltous Dipyrindine Chlorides

BY DAVID P. MELLOR AND CHARLES D. CORYELL

It has been reported by Cox, Shorter, Wardlaw, and Way¹ on the basis of a determination of unit cell dimensions that manganous dipyrindine chloride and the α -form of cobaltous dipyrindine chloride have square *trans*-coördination of pyridine and chlorine about the metal atoms. Complexes of atoms with square bonds have been the object of much interest since this type of structure was first proposed by Werner to explain the existence of certain isomeric platinum compounds.² With the extension of our knowledge about the nature of chemical bonds there has been formulated³ a reliable magnetic criterion by which the existence of square covalent structures for manganous, ferric, ferrous, cobaltic, cobaltous, and nickelous atoms may be determined. It is concluded in this paper that the results of magnetic measurements on the manganous and α -cobaltous dipyrindine chlorides are not compatible with the square coördinated structure proposed by Cox and co-workers, but that they are compatible with an octahedral ionic type of structure.

Magnetic measurements were carried out on the manganese compound by the Gouy method.

(1) E. G. Cox, A. J. Shorter, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937).

(2) A. Werner, *Z. anorg. allgem. Chem.*, **3**, 267 (1893).

(3) L. Pauling, *THIS JOURNAL*, **53**, 1367 (1931).

The forces in mg. (Δw corrected for blank) for a cylindrical tube with water in the upper compartment and air in the lower compartment were for two different field strengths -2.03 and -3.39 . The forces with manganous dipyrindine chloride, twice crystallized from ethanol and packed to a density of 0.99, g./ml., were $+135$ and $+234$, respectively, at 22° against air. With use of an estimated value of -160×10^{-6} for the molecular diamagnetism of the compound and with the assumption of the validity of Curie's law, the calculated values of the magnetic moment are 5.94 and 6.00 Bohr magnetons, the average being 5.97. The expected value of the moment for the manganous atom forming four dsp^2 bonds, essentially covalent and directed toward the corners of a square, is 3.88 plus a small orbital contribution; the expected value for the atom with tetrahedral sp^3 bonds or for the ion is 5.92 magnetons with no orbital contribution (normal state $^6S_{5/2}$). The measurements are in good agreement with the second of these values.

Barkworth and Sugden⁴ have shown that the α -form (violet modification) of cobaltous dipyrindine chloride has a moment of 5.34 Bohr magnetons, and that the β -form (blue modification) has

(4) E. D. P. Barkworth and S. Sugden, *Nature*, **139**, 374 (1937).

a moment of 4.60 magnetons. The expected moment for the cobaltous atom forming dsp^2 bonds is 1.73 plus orbital contribution, and that for the atom forming sp^3 bonds or for the ion is 3.88 plus orbital contribution. We accordingly conclude that the bonds to the cobalt atom are essentially ionic, with an unexpectedly large orbital contribution in the case of the α -form.

A tetrahedral configuration is not compatible with the small dimensions of the c -axes (3.73 and 3.65 Å., respectively) of the manganous and cobaltous compounds, as pointed out by Cox and his co-workers. This configuration is not, however, the only alternative to a square configuration. A reasonable structure for the complexes, one not considered by these workers, can be formulated with each metal ion sharing four coplanar chloride ions in pairs and holding two pyridine molecules at right angles to the plane of the chloride ions. The proposed structure thus contains an ionic octahedral complex with two shared edges. The metal-metal distances in the metal-dichloride chains are calculated⁵ to be 3.7 and 3.6 Å., respectively. The pyridine rings lie in planes the same distance apart. The calculated distances agree with the observed c values to within the accuracy of the ionic radii.

Both the α - and β -forms of the cobalt compound give in organic solvents⁶ identical blue solutions, which have been shown^{1,6} to contain monomeric solute molecules in bromoform, chloroform, and phenol. It is probable that the configuration about the cobalt ion is tetrahedral in these solutions. The fact that the colors of the solutions are nearly the same as that of the solid β -

modification suggests that there is tetrahedral coordination around the metal ions in this solid.

Compounds with a coplanar configuration containing ionic bonds are to be expected only if the electronegative groups are part of a rigid plane structure, as for example in ferriheme chloride (hemin) and ferroheme, in both of which the iron atoms were shown⁷ to be held as ions. It seems very likely that the bonds to beryllium in beryllium phthalocyanin and the bonds to magnesium in chlorophyll are predominantly ionic. The existence of these compounds accordingly is not proof that the metals form square covalent bonds; whereas square coordination with groups which are free to rearrange is an indication of the predominant covalent character of the bonds.^{3,8} Square bonds have not as yet been found in any manganous compound; it has been reported that impure cobalt phthalocyanin⁹ and an impure cobaltous phenanthroline cyanide¹⁰ show magnetic evidence for square bonds, but these observations have not been verified with pure substances.

Summary

The magnetic criterion for bond type indicates that manganese and cobalt atoms in the dipyridine dichloride compounds form ionic bonds rather than covalent dsp^2 bonds. It is suggested that an octahedral ionic type of structure occurs in the manganese and α -cobalt compound and a tetrahedral ionic type occurs in the β -cobalt compound.

PASADENA, CALIF.

RECEIVED APRIL 4, 1938

(7) L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci.*, **22**, 159 (1936).

(8) For a discussion of ionic and covalent character in bonds, see L. Pauling, *THIS JOURNAL*, **54**, 988 (1932).

(9) L. Klemm and W. Klemm, *J. prakt. Chem.*, **143**, 82 (1935).

(10) L. Cambi and A. Cagnasso, *Rend. ist. lombardo sci.*, **67**, 741 (1934).

(5) With the use of the crystal radii of L. Pauling, *THIS JOURNAL*, **49**, 765 (1927), not corrected for the effect of structure.

(6) D. P. Mellor and B. S. Morris, article in press, *Proc. Roy. Soc.*, New S. Wales (1938).