or Raman frequencies of the free NH_3. One might assign these bands to the N→metal stretching frequencies but this assignment is not probable; particularly the band at 7.5 μ cannot be so explained. These are probably associated with deformation vibrations of the NH_3 ligand, due to the formation of N→metal bonds.

In the spectrum of sodium hexanitrocobaltate(III) strong absorption bands associated with the nitro group are observed at 6.8 ~ 7.1, 7.5 and 11.8 μ and a weak band at 12.0 μ. The observed spectrum of the sodium hexanitrocobaltate(III) resembles that of a nitro alkane much more closely than an alkyl nitrite spectrum, indicating that coördination takes place between nitrogen and the central metal of the complex.

In the spectra of the *cis*- and *trans*-dinitrotetramminecobalt(III) chloride the absorption peaks appearing between 7 and 8 μ and at 12 μ are undoubtedly due to the overlapping of the NO_2 ion and the NH_3 ligands, taking into account the fact that the NO_2 ion frequencies are changed to some extent in different salts. It is interesting to note that fewer absorption peaks are present in the spectrum of *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$ than in the *cis* compound. For example, in the region 7 ~ 8 μ, two adjacent peaks appear in the *cis* compound but only one peak appears for the *trans* isomer. This is the natural consequence of the selection rule, since the *trans* complex has a center of symmetry while the *cis* complex does not.

The configurations of the coördination compounds which are in accord with the observed spectra, are octahedral d^2sp^3 hybridization for the *cis* and *trans* isomers, angular d^2 hybridization, and a d^2sp irregular tetrahedron. The latter two structures, which yield weaker covalent bonds, are also in accord with the diamagnetism of the isomers and fulfill the conditions required for the resonance structures.

Acknowledgment.—The generous gift of a set of dies for preparation of the potassium bromide disks from Sister Miriam Michael Stimson, O.P. is greatly appreciated. We are thankful to Brother Columba Curran, C.S.C. and Professor San-ichiro Mizushima for their many helpful suggestions concerning these investigations.

NOTRE DAME, INDIANA

NOTES

The Temperature-Independent Paramagnetism of Ammonium Hexabromoösmate(IV)

BY ROLF B. JOHANNESEN AND ANDREW R. LINDBERG

RECEIVED JUNE 11, 1954

As a part of a program on the investigation of the magnetic properties of compounds of the palladium and platinum triads, we have measured the magnetic susceptibility of ammonium hexabromoosmate(IV), $(NH_4)_2OsBr_6$, over the range of temperatures from 25 to −180°. The Bohr magneton number, $\mu_{eff.}$, defined by the equation $\mu_{eff.} = 2.83 \sqrt{\chi_A T}$, has been found to be 1.51 at 18°, compared with the reported value[1] of 1.49. Moreover, it has been found that χ_A, the susceptibility, is independent of temperature, so that $\mu_{eff.}$ varies as the square root of the absolute temperature. Although the temperature dependence of susceptibility has been measured for some binary halides and oxides of platinum group metals,[2,3] the interpretation of the results is complicated by strong exchange coupling between the paramagnetic centers. Measurements on magnetically dilute compounds are therefore desirable. We believe this to be the first report of the temperature dependence of susceptibility for a platinum group compound which may reasonably be expected to be magnetically dilute.

Kotani[4] has calculated the magnetic moments to be expected for 6-coördinate complex ions in which the central atom has an incomplete shell of d electrons. These calculations depend on the following assumptions: (1) a large intramolecular and crystalline electrostatic energy of cubic symmetry is present; (2) exchange coupling between paramagnetic ions is negligible. The results are presented in the form of equations expressing $\mu_{eff.}$ as a function of A, the spin-orbit coupling coefficient, and T, the absolute temperature. In the general case, $\mu_{eff.}$ is a function of temperature and Curie's law is not obeyed. When there are four d electrons, as in quadrivalent osmium, Kotani's equation leads to the expectation that at low temperatures (up to 800° for this osmium compound) $\mu_{eff.}$ will vary as the square root of the absolute temperature and χ_A will be temperature independent. The temperature independent susceptibility found for ammonium hexabromoösmate(IV) can thus be accounted for on the basis of Kotani's calculations. From our data it is possible to estimate a value of 6400 cm.$^{-1}$ for A, the spin-orbit coupling coefficient. From Kotani's equation it may be estimated that, within the present experimental error of 2%, ammonium hexabromoösmate(IV) will continue to show paramagnetic susceptibility independent of temperature to the limit of its range of stability (170°).

This verification of even a part of Kotani's calculations is interesting in view of the small number of data presently available It would be interesting to subject these calculations to further tests to

---

[1] D. P. Mellor, *J. Proc. Roy. Soc. N.S. Wales*, **77**, 145 (1943).

[2] A. N. Guthrie and L. T. Bourland, *Phys. Rev.*, **37**, 303 (1931).

[3] B. Cabrera and A. Duperier, *Proc. Phys. Soc.*, **51**, 845 (1939).

[4] M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

see if the previously unexplained magnetic behavior of the heavy transition metals[5] can be accounted for entirely on the basis of Kotani's calculations.

Experimental.—Ammonium hexabromoösmate(IV) was prepared from metallic osmium through the tetroxide by the method of Gilchrist.[6] Reagents of analytical grade were used throughout and a spectroscopic analysis of the osmium showed it to be free of other platinum metals. The magnetic susceptibility was measured by the Gouy method with the sample tube suspended inside a large Dewar flask for temperature control.[7] The magnet was a large electromagnet with truncated conical pole pieces and a gap of 2.00 inches. The field strength was varied from 0 to 8,000 oersteds and was measured by means of a calibrated fluxmeter. The susceptibility of powdered cupric sulfate, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, was measured to test the operation of the apparatus. The value of $\mu_{\text{eff.}}$ for cupric ion in this salt was found to be 1.94. This may be compared with reported values of 1.923[8] and 1.920[9] for the same salt.

The susceptibility of ammonium hexabromoösmate(IV) was measured at temperatures of 25.1, −36.3, −47.2, −87.4, −147.4 and −180.2°, and it was found that the susceptibility of osmium(IV), corrected for the diamagnetism of ammonium and bromide ions,[10] was 980×10^{-6} ($\pm 2\%$) c.g.s. units over this entire range. Both the temperature dependence and field strength dependence were zero within the experimental error over the range of values used.

Acknowledgment.—We gratefully acknowledge the helpful advice and encouragement given so generously by Raleigh Gilchrist and Irvin L. Cooter, of this Bureau.

---

(5) J. H. VanVleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Amen House, London, E. C. 4, 1932, pp. 311–315.

(6) R. Gilchrist, *Bur. Standards J. Research*, **9**, 279 (1932).

(7) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943.

(8) J. Reekie, *Proc. Roy. Soc. (London)*, **A173**, 367 (1939).

(9) W. J. DeHaas and C. J. Gorter, *Commun. Phys. Lab. Univ. Leiden*, **19**, No. 210d (1930).

(10) V. C. G. Trew, *Trans. Faraday Soc.*, **37**, 476 (1941).

NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

Liquid Solution of Gallium in Yellow Phosphorus[1,2]

BY ROBERT G. ARMSTRONG[3] AND GEORGE J. ROTARIU

RECEIVED JUNE 28, 1954

The first example of a metal dissolving in a non-metallic liquid by a pure physical process, that of mercury in yellow phosphorus, was discovered by Hildebrand in 1950.[4] The subsequent solubility work[5] revealed that the regular solution theory was able to deal with this system, with an allowance made for the metallic nature of the mercury. One would expect the metallic nature of the mercury to lead to a larger excess free energy and therefore to a smaller solubility; this was indeed the case.

We have investigated the system of liquid gallium in yellow phosphorus at 45° with the aim of finding a second system in which a liquid metal dissolves in a non-metallic liquid. Although the theory predicts a solubility of 10^{-30} g. Ga/3 cc. P_4, it was felt that enough gallium might dissolve (if this system could not be handled by the theory) to make its presence detectable. The pertinent physical constants are summarized in Table I; the data are taken from reliable sources.[6]

TABLE I

PHYSICAL CONSTANTS

	P_4	Hg	Ga
M.p., °C.	44.1	−38.9	29.75
B.p., °C.	280.5	357	1983
d_{25}	1.76	13.55	5.9
V_{25}	70.4	14.8	11.8
Resistivity (micro-ohms cm.)	10^{11}	95.8	27
δ_{25}	14.5	30.7	74

Gallium has been reported[7] to form a phosphide, GaP, but only under extreme conditions; when Ga(OH)_3 is heated in a P_4 vapor atmosphere (diluted with H_2) at 500°, the orange-yellow GaP is formed. We have found that liquid gallium (Alcoa, 99.95%) could be kept in contact with liquid phosphorus at 45° almost indefinitely with no discoloration of the shiny metallic surface of gallium and with no trace of an orange-yellow substance. We did find that a trace of a substance of this color was formed when the mixture was kept at 98° for 15 minutes. Since our work was to be done at 45° or lower it seemed unlikely any phosphide would form.

We conclude, on the basis of the following evidence, that gallium metal dissolves in yellow phosphorus by a physical process, to the extent of 0.01 to 0.1 µg. of gallium per ml. of P_4 at 45°.

Ga Metal Dissolves.—(1).—When samples of phosphorus (saturated with Ga; filtered through a medium porosity scintered glass disc) were burned in air and the residue excited by a 110 v. a.c. carbon arc, the 4033 Å. Ga I emission line (Gaertner Monochrometer) was observed. Similar tests with the water and phosphorus used failed to reveal any line at 4033 Å.

(2).—Metallic beads of gallium metal were isolated from six samples of Ga-saturated P_4. The freezing and washing away of the P_4 with CS_2 of such samples revealed the presence of tiny metallic-like beads (45–260 × magnification) which could be rolled about and indented with a needle probe. These beads were supercooled with ice to 0°, frozen with Dry Ice and remelted at about 30° with an electric wire. It should be pointed out that traces of Ga_2O_3 are undoubtedly present in suspended or dissolved form also in the P_4, although we have never observed any white or gray residue with this procedure. Positive 8-hydroxyquinoline tests[8] confirmed the presence of gallium. These metallic beads were also isolated by a high vacuum distillation (10^{-5} mm.) of the P_4 at 55°.

Solubility between 0.01–0.1 µg. Ga/ml. P_4. (1).—The upper limit of 0.1 µg. is given by the failure of observing any absorption at 392.5 mµ for the gallium-quinolinol present when tested according to the procedure of Moeller and Cohn[9] with the Beckmann Model DU Spectrophotometer. These authors have shown that the minimum detectable limit is 0.1 µg. of gallium per ml. of CHCl_3 extracting solvent. These samples which did not show an absorption spectra, when evaporated to dryness and the residue examined spectrographically, *did* reveal the 4033 Å. Ga I line.

---

[1] This work was supported by a grant from Research Corporation.

[2] Presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

[3] This is a portion of the work submitted in the thesis for the M.S. degree to the Dept. of Chemistry, Loyola University, Chicago 26, Ill.

[4] J. H. Hildebrand, "Abstracts of Papers," 118th Meeting, American Chemical Society, Chicago, Ill., Sept. 1950, p. 13Q.

[5] G. J. Rotariu, E. Schramke, T. S. Gilman and J. H. Hildebrand, THIS JOURNAL, **73**, 2527 (1951).

[6] G. H. Wagner and W. H. Gitzen, *J. Chem. Educ.*, **29**, 162 (1952); N. A. Lange, "Handbook of Chemistry," 8th ed., 1952; the molar volumes and solubility parameters δ, from J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 3rd ed., 1950.

[7] E. Einecke, "Das Gallium," Leipzig, 1937, p. 97, and in Gmelin's "Handbuch," Vol. 36, 1936, p. 95.

[8] E. B. Sandell, *Anal. Chem.*, **19**, 63 (1947); *ibid.*, **13**, 844 (1941).

[9] T. Moeller and A. J. Cohen, *ibid.*, **22**, 686 (1950).