was fractionally distilled through an 11 × 350 mm. column packed with glass beads. The properties of the product are given in Table I.

Anal.[7] Calcd. for $C_9H_{29}N_3Si_4$: C, 37.06; H, 10.02; N, 14.40; Si, 38.52. Found: C, 36.68; H, 9.72; N, 14.10; Si, 38.32.

Acknowledgment.—The authors wish to express their appreciation to Dr. J. J. Downs for the preparation and interpretation of the n.m.r. spectra.

(7) Analyses by Spang Microanalytical Laboratory, Box 1111, Ann Arbor, Michigan.

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Magnetic Studies of Mixed Ligand Complexes of Iron(II)

BY W. A. BAKER, JR., AND H. M. BOBONICH

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Mixed ligand complexes of Fe(II) having the general formula $[Fe(phen)_2X_2]$ (hereafter referred to as the bis complexes; phen = 1,10-phenanthroline) have been reported by a number of investigators.[1-3] Basolo and Dwyer[1] prepared the chloride and reported it to be high spin with μ = 5.3 B.M. at room temperature. Previously, Klemm[2] had reported the bromide and iodide to be diamagnetic. In view of the well accepted order of ligand field strengths for halide ions, these results seem unlikely unless there are important structural differences between the chloride on the one hand and the bromide[4] and iodide on the other.

Schilt[3] has also prepared the analogous cyanide complex and finds it to be low spin but exhibiting paramagnetism corresponding to a room temperature moment of 0.68 B.M. The moment he suggests is due to temperature-independent paramagnetism which is known to be appreciable for low spin Co(III) complexes and is expected for other d^6 systems.[5]

It is the purpose of this note to report results which resolve the apparent anomaly found for the halide complexes, a new method for their preparation, a thiocyanate complex not previously reported,[4] as well as data on the low spin cyanide complex.

Experimental

Preparation of $[Fe(phen)_2X_2]$.—$[Fe(phen)_2(CN)_2]\cdot 2H_2O$ was prepared by the method of Schilt.[3] *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})(CN)_2(H_2O)_2$: C, 61.92; H, 4.00; N, 16.67. Found: C, 62.13; H, 3.86; N, 16.86.

For the preparation of the bis-halides, the pyrolysis techniques of Klemm[2] and Basolo and Dwyer,[1] *i.e.*, the heating of the appropriate $[Fe(phen)_3]X_2$ (hereafter referred to as the tris complexes) under vacuum was attempted. Although this method seemed to give some of the desired product, the analyses on different portions of the same sample were slightly variable and the products were not homogeneous in appearance. Therefore, this method was used only in the case of the iodide, for which other methods of preparation were unsuccessful.

The method used for the other halides as well as the thiocyanate was to suspend the appropriate tris complex in a moderate boiling inert solvent under reflux conditions. The suspended material gradually changed from the characteristic red color of the tris complex to a homogeneous blue. Periodic checks of the magnetic susceptibility indicated a change from low spin to high spin. The suspended material was filtered, washed with pure refluxing solvent, and dried under vacuum previous to analysis and magnetic measurements.

$[Fe(phen)_2I_2]$ was prepared by heating $[Fe(phen)_3]I_2$ under vacuum at 186° for about 7 days. *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})I_2]$: C, 43.01; H, 2.41; N, 8.35. Found: C, 43.44; H, 2.44; N, 8.36.

$[Fe(phen)_2Cl_2]$ was prepared by suspending $[Fe(phen)_3Cl_2]$ in CCl_4 and refluxing for 36 hr. *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})Cl_2]$: C, 59.16; H, 3.28. Found: C, 59.64; H, 3.39.

$[Fe(phen)_2Br_2]$ was prepared by suspending $[Fe(phen)_3]Br_2$ in methylcyclohexane and refluxing for 100 hr. *Anal.* Calcd. for $[Fe(C_{24}N_4H_{16})Br_2]$: C, 50.04; H, 2.80; N, 9.72. Found: C, 49.88; H, 2.78; N, 9.34.

$[Fe(phen)_2(SCN)_2]$ was prepared by refluxing $[Fe(phen)_3]\cdot(SCN)_2$ in CCl_4 for 48 hr. *Anal.* Calcd. for $[Fe\ (C_{12}N_4H_{16})(SCN)_2]$: C, 58.65; H, 3.03. Found: C, 58.33; H, 2.92.

Magnetic Measurements.—Susceptibilities were obtained using a Gouy balance equipped for measurements over the range 77–300°K. $Hg[Co(SCN)_4]$ was used as a calibrant. Diamagnetic corrections were made using values given by Figgis and Lewis.[6] All compounds were measured at three field strengths and showed no field dependence. The moments are accurate to at least ±0.05 B. M. at the high values and ±0.10 at the low values.

Microanalyses.—C, H, and N analyses were performed by the Schwaazkopf Microanalytical Laboratories, Woodside, N. Y.

Discussion

As can be seen from Table I, the paramagnetism of the bis-cyanide is in fact temperature independent. The values of χ_{corr}^M are reasonably constant over a 200° range. Although there is some deviation in the observed susceptibilities (see Table I), these are readily understood when it is realized that the forces involved in the measurements on the bis-cyanide are of the order of 1 mg. The results given represent a typical set of values obtained for a given sample. Values for other samples show the same general results; that is, susceptibilities in the range 200 ± 50 × 10^6.

TABLE I

MAGNETIC DATA FOR $[Fe(phen)_2(CN)_2]\cdot 2H_2O$

T, °K.	χ_{corr}^M (× 10^6)	μ_{eff}, B.M.
297	235	0.74
257	235	.70
193	159	.50
156	185	.48
112	243	.46

The data for the bis-halides are given in Table II.

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(1) F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, **76**, 1454 (1954).

(2) V. W. Klemm, *et al.*, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

(3) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(4) K. Madĕja and E. Konig, *J. Inorg. Nucl. Chem.*, **25**, 377 (1963), have recently reported the preparation of the bis-bromide and thiocyanate and find both to be high spin, in agreement with our results.

(5) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

(6) B. N. Figgis and J. Lewis, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

TABLE II

MAGNETIC DATA FOR $[Fe(phen)_2X_2]$ AT 25°

X	μ_{eff}, B.M.
CN^-	0.74
Cl^-	5.26
Br^-	5.16
I^-	5.14
SCN^-	5.21

As expected, all of the halides are high spin, with the room temperature moment about that expected for a d^6 system. The previously reported values for bromide and iodide[2] are in error and probably arose, as has previously been suggested,[7] from the fact that under the conditions at which the bis compounds were supposedly prepared, a tris compound is merely dehydrated rather than converted to the bis.

The bis-thiocyanate is also observed to be high spin, as is indicated in Table II.

It is of interest to note that in attempting to prepare the bis-iodide by refluxing the tris-iodide in CCl_4, the moment of the sample rapidly changed to high spin values, but closer investigation showed that the high moment was due to the bis-chloride rather than the iodide, indicating a rapid exchange between the complex and solvent.

At the present time we are carrying out more extensive magnetic and spectral studies on these and related compounds. We also plan to investigate the nature of the halide exchange between the iodide and CCl_4.

Acknowledgment.—The authors wish to thank the National Science Foundation for support under grant NSF-G14529.

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[7] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

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The Reaction of Borazine with Phenylmagnesium Bromide[1]

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The reaction of borazine[2] with phenylmagnesium bromide has never been reported. However, Smalley and Stafiej[3] have shown that the hydrogen atoms attached to boron in 1,3,5-trimethylborazine may be replaced by alkyl or aryl groups using Grignard reagents. It seemed likely that similar reactions would occur with the parent compound, borazine. Such reactions might offer a convenient synthetic approach to mono- and di-, alkyl and aryl, borazine derivatives substituted only on the boron atoms. The preparation of phenylborazine derivatives from borazine and phenylmagnesium bromide was therefore attempted. 2-Phenylborazine and 2,4-diphenylborazine were isolated and characterized. A small quantity of 2,4,6-triphenylborazine was also obtained.

Experimental

Materials.—Reagent grade solvents were dried over sodium wire before being used.

The borazine was prepared by the reduction of 2,4,6-trichloroborazine with sodium borohydride using the dimethyl ether of tetraethylene glycol as a solvent.[4]

A 3 *M* solution of phenylmagnesium bromide in ether was obtained from Arapahoe Special Products, Inc., of Boulder, Colorado. This solution was diluted with dry ether to one approximately 1 *M* in phenylmagnesium bromide and standardized.

Analytical Methods and Apparatus.—Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. All other analytical methods and apparatus were identical with those described in an earlier publication.[5]

Description of Experiment and Separation of the Products.—A 300-ml. flask, equipped with a magnetic stirrer and fitted with an addition funnel, was attached to a vacuum system. In a typical preparation 4.0 g. (0.05 mole) of borazine was distilled into the reaction flask from the vacuum system. Dry ether (175 ml.) followed by 48 ml. of 1.05 *M* phenylmagnesium bromide in ether (0.05 mole) were then added by means of the addition funnel. The addition of phenylmagnesium bromide was carried out over a 30-min. period with constant stirring. The resulting solution was allowed to stand at room temperature under an atmosphere of nitrogen overnight.

The flask was removed from the vacuum system and 50 ml. of dry cyclohexane was added to the reaction mixture. Ether was removed by distillation at atmospheric pressure and the resulting cyclohexane solution decanted from the solid that separated. The cyclohexane was removed from this solution by evaporation at room temperature on a vacuum system. About 6 g. of a fluffy white powder remained. This white powder was found to be a mixture of 2-phenylborazine, 2,4-diphenylborazine, 2,4,6-triphenylborazine, and some magnesium salts. It was possible to separate the three borazines by fractional sublimation.

The reaction residue was placed in a vacuum sublimator and fractions were collected at 40, 70, 100, 130, and 165°. Heating was continued for about 48 hr. at each temperature. Several grams of a nonvolatile white solid remained in the sublimator after 48 hr. at 165°. A solution of this material in water gave positive tests for bromine and magnesium.

The material collected at 40, 100, and 165° was, respectively, crude 2-phenylborazine, 2,4-diphenylborazine, and 2,4,6-triphenylborazine. The material collected at 70° was 2-phenylborazine containing some 2,4-diphenylborazine while the material collected at 130° was 2,4-diphenylborazine containing some 2,4,6-triphenylborazine. The crude 2-phenylborazine, 2,4-diphenylborazine, and 2,4,6-triphenylborazine were purified by repeated vacuum sublimations at 40, 100, and 165°, respectively. Purified 2-phenylborazine (1.5 g., 19% yield based on phenylmagnesium bromide), purified 2,4-diphenylborazine (0.9 g., 15% yield), and purified 2,4,6-triphenylborazine (0.2 g., 4% yield) were obtained.

Description.—Both 2-phenylborazine and 2,4-diphenylborazine form colorless crystals when sublimed. 2-Phenylborazine melts

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[1] Abstracted from a part of a Ph.D. thesis submitted by P. C. Moews' Jr., to the Department of Chemistry, Cornell University, 1960.

[2] In line with the recommendations of the Committee on the Nomenclature of Boron Compounds, the term borazine is used in this paper rather than the older term borazole. A numerical prefix precedes the name of the substituent and designates its location on the ring; numbering the ring begins with the nitrogen atom.

[3] J. H. Smalley and S. F. Stafiej, *J. Am. Chem. Soc.*, **81**, 582 (1959).

[4] L. F. Hohnstedt and D. T. Haworth, *ibid.*, **82**, 89 (1960).

[5] A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *ibid.*, **83**, 1337 (1961).