theorem of corresponding solutions[13] this can only mean essentially no change in the immediate surroundings of the rare earth ions. Therefore the change of the a parameter with dielectric constant indicates that the purely electrostatic approach of Bjerrum is inadequate for these systems. We are faced again with the difficulty of naming an electrolyte that does not obey the criteria of the Onsager–Fuoss or Bjerrum approaches. At the present time I can only call these hexacyanocobaltates of the rare earths incompletely dissociated electrolytes, with no solid operational definition to clarify this title.

As more data accumulate it seems more and more apparent that different experimental approaches are giving us different association parameters for the same salts. These differences seem partially inherent in the methods and theories involved and not merely experimental artifacts. It would be of great value if the "association" of some symmetrical electrolyte, preferably of the 2–2 variety, could be measured by a coöperating group of researchers using four or five of the most important methods and a very exhaustive study made of the results.

A plot of $-\log K$ *versus* $1/D$ is a straight line for all four of these salts. However, the slope is less than that predicted by the Bjerrum equation. To obtain the Bjerrum line for this comparison a was assumed constant and equal to the pure water value. A plot of $-\log K$ *versus* cation radius is also a straight line within experimental error for lanthanum, neodymium and samarium. It is not possible to say much about the off-line position of yttrium without association data for some of the yttrium-group rare earths. Although yttrium is not a true rare earth its ionic radius lies between those of dysprosium and holmium. This leads to a strong similarity to the heavy rare earths both in its solution chemistry[14] and in complex formation.[15] It should be noted also that although the K and a values change in the order La, Nd, Sm, Y; the Λ_0 values and phoreograms fall in the order La, Nd, Y, Sm.

Acknowledgments.—The author wishes to acknowledge the loan by Prof. R. W. Parry of the electrical conductance equipment used in this work.

(13) J. Bjerrum and C. K. Jørgensen, *Acta Chem. Scand.*, **7**, 951 (1953).

(14) Ref. 9, pp. 327, 330.

(15) (a) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, THIS JOURNAL, **75**, 4196 (1953); (b) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *ibid.*, **76**, 2557 (1954).

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Complexes of Iron(II), Cobalt(II) and Nickel(II) with Biacetyl-bis-methylimine, 2-Pyridinal-methylimine and 2,6-Pyridindial-bis-methylimine

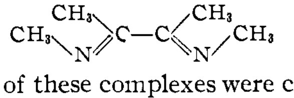
BY PAUL E. FIGGINS AND DARYLE H. BUSCH

RECEIVED JULY 6, 1959

The synthesis of the series of octahedral complexes formed by iron(II), cobalt(II) and nickel(II) with biacetyl-bis-methylimine (BMI), 2-pyridinal-methylimine (PMI) and 2,6-pyridindial-bis-methylimine (PdMI) has been completed, and seven of the complexes are reported for the first time. The magnetic moments have been determined at room temperature. The values observed for the nickel(II) complexes are typical of spin-free, regular octahedral structures. The iron(II) complexes are essentially diamagnetic, exhibiting small residual paramagnetisms as is commonly found for spin-paired octahedral species involving d^6 ions. The moments for the cobalt(II) complexes are unusually low in value (2.31, 2.98 and 4.39 Bohr magnetons). It is suggested that these compounds exist as equilibrium mixtures of isomeric spin-free and spin-paired ions.

Introduction

In 1953, Krumholz[1] prepared the iron(II) complexes with α-diimines, of which biacetyl-bis-methylimine (structure I) serves as an example.[2]



I

The spectra of these complexes were compared with those of tris-(*o*-phenanthroline)-iron(II) and tris-(2,2′-bipyridine)-iron(II), and it was concluded that these α-diimine complexes were of the same type as the more familiar species. Krumholz found that only the N,N′-bis-methylimines formed this type of complex; *i.e.*, biacetyl-bis-anil, biacetyl-bis-benzilimine and biacetyl-bis-ethylimine do not form the permanganate colored iron(II) complexes. This observation is explained readily in terms of the great steric requirements of the relatively large alkyl or aryl groups. The interpretations of Krumholz were confirmed in later studies[3,4] in which it was shown that $[Fe(BMI)_3]\ I_2$ is spin-paired (essentially diamagnetic). Although a number of complexes have been reported for the benzil and phenyl analogs of BMI,[5] no metal ion other than iron(II) previously has been incorporated in complexes with simple aliphatic α-diimines. Further, the cobalt(II) and nickel(II) complexes reported here represent the only examples of octahedral complexes formed by α-diimines, other than those prepared by Krumholz.

During the course of investigations directed toward the verification of the nature of the complexes of iron(II) with α-diimines,[3] the iron(II) complex of 2-pyridinal-methylimine (structure II) was prepared. This ligand provides a simple structural link between 2,2′-bipyridine (structure III) and the α-diimines (structure I), being constituted of one functional group of each type. The results of studies of the visible, ultraviolet and infrared spectra, together with the diamagnetism of this complex, completed the synthesis and characterization of the series of octahedral, diamagnetic iron(II) complexes which were labeled, because of

(1) P. Krumholz, THIS JOURNAL, **75**, 2163 (1953).

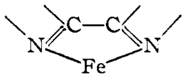
(2) These abbreviations will be used extensively: BMI, biacetyl-bis-methylimine; PMI, 2-pyridinal-methylimine; PdMI, 2,6-pyridindial-bis-methylimine.

(3) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **78**, 1137 (1956).

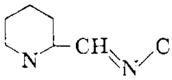
(4) K. Sone, *Naturwissenschaften*, **5**, 104 (1956).

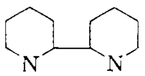
(5) G. Bahr, *Z. anorg. allgem. Chem.*, **267**, 137, 161 (1951).

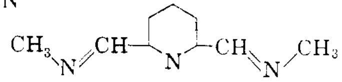
their spectral properties, as compounds of the iron(II)–methine chromophore. The series [Fe(*o*-phen)$_3$] I$_2$, [Fe(dipy)$_3$] I$_2$, [Fe(PMI)$_3$] I$_2$, [Fe(BMI)$_3$] I$_2$ involves complex cations containing three bidentate ligands and characterized by the chelate ring



As listed, the ligands in successive complexes decrease in the number of aromatic rings in their structures, the first member, *o*-phenanthroline (*o*-phen), having three fused rings, while the last member is alicyclic. It has been shown[3] that the maximum absorption in the visible spectrum shifts to longer wave lengths as the number of rings in the structure of the ligand decreases. This trend provides inferential support for hypotheses relating to the importance of pi-bonding in these compounds. If the chelate ring is considered to be an aromatic ring, the effectiveness of the delocalization of electrons in this ring should be at a maximum in the absence of fused rings. The infrared spectra of this series of iron(II) complexes provided the first direct evidence of the presence of very important conjugative effects in the chelate rings.[3] More recently, a number of additional complexes have been prepared with PMI and related ligands,[6–8] and a few complexes have been reported with tridentate ligands analogous to 2,6-pyridinidial-bis-methylimine (structure IV).[8,9] Despite these recent studies, the cobalt(II) and nickel(II) complexes with PMI and PdMI are reported for the first time here.


II


III


IV

Experimental

Materials.—2-Pyridinaldehyde was obtained from the Aldrich Chemical Company and purified by distillation (b.p. 64° (9 mm.)) when necessary. 2,6-Pyridindialdehyde was obtained from Aldrich Chemical Company and used without further purification. Technical grade sodium fluoroborate was obtained from Baker and Adamson and purified by recrystallization from water. Potassium iodide, iron(II) chloride 4-hydrate, cobalt(II) chloride 6-hydrate, nickel(II) chloride 6-hydrate, biacetyl and 40% aqueous methylamine were the usual reagent chemicals and were not purified.

2-Pyridinal-methylimine.—2-Pyridinal-methylimine was prepared by the method of Bahr and Doge.[6] The product was a colorless liquid which became yellow after a few minutes. *Anal.* Calcd. for $C_7H_8N_2$: C, 70.0; H, 6.7; N, 23.4. Found: C, 69.9; H, 6.8; N, 23.2. After storage for five weeks at 0°, some crystals were observed in the liquid 2-pyridinal-methylimine and approximately 50 mg. of white crystals was isolated. Within four days, much of the remaining liquid had crystallized and was separated by filtering and washed with ether. The infrared spectra of these fractions were identical. Within a week, the remainder of the liquid 2-pyridinal-methylimine had crystallized. The melting point of the crystalline material was 208–210°. The molecular weight as determined by the Rast method[10] was 242; that calculated for pyridinal-methylimine is 120. *Anal.* Found: C, 70.5; H, 6.2; N, 23.3. Only the liquid material was utilized in the synthesis of complexes.

2,6-Pyridindial-bis-methylimine.—Twenty-five milliliters (excess) of 40% aqueous methylamine solution was added, very slowly at first and without cooling, to 19.5 g. (0.145 mole) of 2,6-pyridindialdehyde. The resulting brown solution was allowed to stand for 4 hr. before the excess methylamine was removed under reduced pressure (water aspirator). Upon fractional distillation, the water fraction was obtained at 44° (68 mm.) and a very small fraction at 60° (3 mm.) both of which were discarded. The main fraction came over at 92–94° (3 mm.) and was a colorless oil. During the distillation, especially at the higher temperatures, the solution in the distilling pot became very black indicating either decomposition or polymerization of the ligand. The free ligand has a melting point of 23° and was purified further by fractional crystallization. The yield was 8.31 g. (36%) of white, elongated crystals. *Anal.* Calcd. for $C_9H_{11}N_3$: C, 67.1; H, 6.9; N, 26.0. Found: C, 66.8; H, 7.1; N, 25.8.

Tris-(2-pyridinal-methylimine)-cobalt(II) Fluoroborate.—Three and thirty-two hundredths grams (0.014 mole) of cobalt(II) chloride 6-hydrate was dissolved in 20 ml. of air-free water (nitrogen) in a 50° water-bath. Five milliliters (0.042 mole) of 2-pyridinal-methylimine was mixed with 10 ml. of air-free water, and, over a period of 30 minutes, the solution was added dropwise, with stirring, to the solution of cobalt(II) chloride. The resulting dark reddish brown solution was stirred for an additional 90 minutes while the temperature of the water-bath was maintained at, or below, 50°. If a brown oil was formed when 5 g. of sodium fluoroborate was added, the solution was warmed until the oil dissolved. Cooling to 0° overnight produced a brownish black crystalline product which was washed twice with 2-ml. portions of cold water. The yield was 5.0–5.3 g. (60–64%). The crude product was recrystallized from 20 ml. of water by dissolving at 50° and cooling (75% recovery). *Anal.* Calcd. for $Co(C_7H_8N_2)_3(BF_4)_2$: C, 42.5; H, 4.1; N, 14.2; Co, 9.9. Found: C, 42.3, 42.2; H, 4.2, 4.1; N, 14.0, 14.2; Co, 10.3.

Tris-(2-pyridinal-methylimine)-nickel(II) Fluoroborate.—The nickel complex was formed in the same manner as the cobalt complex, except for the absence of the protective nitrogen atmosphere, using 3.32 g. (0.014 mole) of nickel(II) chloride 6-hydrate, 5 ml. (0.042 mole) of 2-pyridinal-methylimine and 5 g. of sodium fluoroborate. In solution, the complex is a lighter brown than the cobalt complex, and, in the solid state, it exists as a tan crystalline powder. The yield of crude product was 5.84 g. (70%). This product was recrystallized by dissolving in 22 ml. of water at 50° and cooling. The recrystallized product was dried *in vacuo* over P_2O_5 (75% recovery). *Anal.* Calcd. for $Ni(C_7N_8N_2)_3(BF_4)_2$: C, 42.5; H, 4.1; N, 14.2; Ni, 9.9. Found: C, 42.2, 42.4; H, 4.2, 4.2; N, 14.1, 14.5; Ni, 10.2.

Bis-(2,6-pyridindial-bis-methylimine)-iron(II) Iodide.—Four and twenty-four hundreths grams (0.0314 mole) of 2,6-pyridindialdehyde was placed in a beaker, slurried with 5 ml. of absolute ethanol, and 10 ml. of a 40% methylamine solution was added slowly, with stirring. Three and one-tenth grams (0.0157 mole) of iron(II) chloride 4-hydrate was dissolved in 10 ml. of air-free water and filtered into the solution of ligand. The solution became a deep permanganate color. Precipitation began as soon as 7 g. of potassium iodide was added to the solution. After cooling to 0°, the glittering black product was filtered and washed with 4 ml. of cold water. The yield was 7.80 g. (78%), and the product was recrystallized by dissolving in 40 ml. of water at 50°, adding 4 g. of potassium iodide and cooling. The product was dried *in vacuo* over P_2O_5 (80% recovery). *Anal.* Calcd. for $Fe(C_9H_{11}N_3)_2I_2 \cdot 2H_2O$: C, 32.3; H, 3.9; N, 12.6; Fe, 8.4. Found: C, 32.4, 32.6; H, 3.8, 3.7; N, 12.2, 12.4; Fe, 8.3, 8.5.

Bis-(2,6-pyridindial-bis-methylimine)-cobalt(II) Iodide (Method One).—Three and forty-one hundredths grams (0.0209 mole) of 2,6-pyridindial-bis-methylimine was dissolved in 6 ml. of ethanol. To this solution was added 2.48 g. (0.0105 mole) of cobalt(II) chloride 6-hydrate in 10 ml. of water. Seven grams of potassium iodide was added with stirring to the resulting dark reddish black solution. The solution was filtered after cooling to 0° and the black crystals washed with 4 ml. of alcohol before drying *in vacuo* over P_2O_5. The yield was 6.18 g. (93%). The crude product was recrystallized from 20 ml. of water by heating to 50°, filter-

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[6] G. Bahr and H. G. Doge, *Z. anorg. allgem. Chem.*, **291**, 117 (1957).

[7] G. Bahr and Thamlitz, *ibid.*, **282**, 3 (1955).

[8] R. C. Stoufer and D. H. Busch, THIS JOURNAL, **78**, 6016 (1956).

[9] F. Lions and K. V. Martin, *ibid.*, **79**, 2733 (1957).

[10] K. Rast, *Ber.*, **55**, 1051, 3727 (1922).

ing, then adding 2 g. of potassium iodide and cooling. The product was dried *in vacuo* over P_2O_5 (59% recovery). *Anal.* Calcd. for $Co(C_9H_{11}N_3)_2I_2 \cdot H_2O$: C, 33.1; H, 3.7; N, 12.9. Found: C, 33.4, 33.4; H, 3.6, 3.4; N, 12.6, 12.6.

Bis-(2,6-pyridindial-bis-methylimine)-cobalt(II) Iodide (Method Two).—A slurry was made of 4.32 g. (0.032 mole) of 2,6-pyridindialdehyde in 5 ml. of ethanol. Five milliliters of 40% methylamine solution was added slowly to avoid excessive heating of the solution. After stirring for a few minutes, 3.89 g. (0.016 mole) of cobalt(II) chloride 6-hydrate in 10 ml. of water was added, and then 20 g. of potassium iodide. The solution was heated in a 50° water-bath, with stirring, for 30 minutes, before cooling overnight. Upon filtering, a sparkling black, fine powder was obtained and washed with ethanol and ether and then air dried. The yield of the crude product was 6.47 g. (63%). This was purified by dissolving in 15 ml. of water at 50° and filtering. Before cooling, 1.5 g. of potassium iodide was added (46% recovery). *Anal.* Calcd. for $Co(C_9H_{11}N_3)_2I_2 \cdot H_2O$: C, 33.1; H, 3.7; N, 12.9. Found: C, 33.4, 33.2; H, 3.6, 3.4; N, 12.6, 12.4.

Bis-(2,6-pyridindial-bis-methylimine)-nickel(II) Iodide.—A slurry was made of 4.32 g. (0.032 mole) of 2,6-pyridindialdehyde in 5 ml. of ethanol. Ten milliliters (excess) of 40% methylimine solution was added slowly with stirring, followed by a solution of 3.80 g. (0.016 mole) of nickel(II) chloride 6-hydrate in 10 ml. of water. This solution was poured onto 8 g. of solid potassium iodide and the mixture was maintained under reduced pressure to remove the excess methylamine. Upon cooling and filtering, a tan product was obtained which was washed with 4 ml. of ethanol, then ether, and dried in a vacuum desiccator. The yield of the crude product was 4.27 g. (42%). The crude product was recrystallized by dissolving in 15 ml. of water at 50°, filtering and adding 1.5 g. of potassium iodide. The brown crystals, which were obtained by cooling the solution to 0°, were washed with 2 ml. of ethanol and dried *in vacuo* over P_2O_5 (89% recovery). *Anal.* Calcd. for $Ni(C_9H_{11}N_3)_2I_2 \cdot H_2O$: C, 33.1; H, 3.7; N, 12.9; Ni, 9.0. Found: C, 33.3, 33.4; H, 3.6, 3.5; N, 12.6, 12.8; Ni, 9.3, 9.7.[11]

Tris-(biacetyl-bis-methylimine)-cobalt(II) Iodide.—Four and seventy-six hundredths grams (0.02 mole) of cobalt(II) chloride 6-hydrate was dissolved in 5 ml. of water. With a stream of nitrogen gas blowing on the surface of the solution to provide a protective atmosphere, 10 ml. of 40% aqueous methylamine solution was added slowly. Because of the heat evolved, water cooling was necessary when 5.1 ml. (0.06 mole) of biacetyl was added slowly. To ensure complete reaction of the biacetyl, an additional 2 ml. of methylamine solution was added. A fine black powder was obtained when 7 g. of potassium iodide was added and the solution cooled to 0°. This crude product was dissolved in 20 ml. of a 1:1 ethanol–water solution at 55°, filtered and recrystallized by cooling to 0°. The shiny black crystals of product were washed with ethanol and dried *in vacuo* over P_2O_5. The yield was 2.49 g. (19%). *Anal.* Calcd. for $Co(C_6H_{12}N_2)_3I_2 \cdot H_2O$: C, 32.4; H, 5.7; N, 12.6. Found: C, 32.2, 31.9; H, 5.4, 5.4; N, 12.4, 12.4.

Tris-(biacetyl-bis-methylimine)-nickel(II) Iodide.—Four and seventy-six hundredths grams (0.020 mole) of nickel(II) chloride 6-hydrate was dissolved in 5 ml. of water and 12 ml. of 40% aqueous methylamine solution was added slowly. This blue solution turned to a dark brown, and a great deal of heat was evolved as 5.1 ml. (0.06 mole) of biacetyl was added slowly. The excess methylamine was removed under reduced pressure, and 7 g. of potassium iodide was added before the solution was cooled to 0°. A very fine brown powder, which was difficult to filter, was obtained and dried over P_2O_5. The yield of the crude product was 6.8 g. (52%). The crude product was dissolved in 20 ml. of a 1:1 ethanol–water solution and filtered. A greenish, gelatinous material, which was left on the filter, may account for the difficulty in filtering. Upon cooling the ethanol–water solution to 0°, a nicely crystalline product was obtained. After drying *in vacuo* over P_2O_5, the yield was 4.5 g. (66% recovery). *Anal.* Calcd. for $Ni(C_6H_{12}N_2)_3I_2$: C, 33.3; H, 5.6; N, 13.0. Found: C, 33.4; H, 5.9; N, 13.1.

Magnetic Measurements.—The magnetic moments of the complexes of 2-pyridinal-methylimine, 2,6-pyridindial-bis-methylimine and biacetyl-bis-methylimine were obtained by the Gouy method, using an Ainsworth semimicro-analytical balance. The values given by Selwood[12] were used for the diamagnetic susceptibilities of the anions. Pascal's constants[13] were used in calculating corrections for the diamagnetism of the ligands. The values utilized are given in Table I. Magnetic data for the complexes are listed in Table II.

TABLE I

MOLAR SUSCEPTIBILITIES OF LIGANDS AND ANIONS

Ligand or anion	$\chi_M \times 10^6$
2-Pyridinal-methylamine	−65
2,6-Pyridindial-bis-methylimine	−79
Biacetyl-bis-methylimine	−35
Fluoroborate ion	−39
Iodide ion	−52
Water	−13

TABLE II

CORRECTED MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF METAL IONS

Compound[a]	Cor. $\chi_M \times 10^6$	μ_{eff}
$[Ni(PMI)_3](BF_4)_2$	+3979	3.12
$[Co(PMI)_3](BF_4)_2$	+7993	4.39
$[Fe(PdMI)_2]I_2 \cdot 2H_2O$	+ 209	0.71
$[Ni(PdMI)_2]I_2 \cdot H_2O$	+4292	3.22
$[Co(PdMI)_2]I_2 \cdot H_2O$	+2221	2.31
$[Ni(BMI)_3]I_2$	+4355	3.24
$[Co(BMI)_3]I_2 \cdot H_2O$	+3640	2.98

[a] Abbreviations used: PMI, 2-pyridinal-methylimine; PdMI, 2,6-pyridindial-bis-methylimine; BMI, biacetyl-bis-methylimine.

Results

Complexes of 2-Pyridinal-methylimine.—Previous investigators have reported 2-pyridinal-methylimine complexes with a number of metal ions. However, from among the Triad of first row Group 8 elements, only the iron(II) complex has previously been prepared. During the course of this investigation, the complexes of cobalt and nickel with PMI were prepared and their magnetic moments were determined. The free ligand is an oil having a boiling point very close to that of the aldehyde, 64° (9 mm.) and 67° (10 mm.), respectively. In order to obtain a pure product, excess methylamine must be utilized during the synthesis. The liquid appears to be completely miscible with water and ethanol, but it is immiscible with ether. The complexes of PMI form instantly when aqueous solutions of the ligand and a metal ion are mixed. However, some difficulty was encountered in obtaining crystalline products. The procedures given represent the culmination of many experiments carried out under a variety of conditions.

The iron(II) complex of 2-pyridinal-methylimine is quite similar to the iron(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline. The complex is destroyed only slowly in the presence of strong acid, and the color is slightly less intense than that of the complex of 1,10-phenanthroline but more intense than the 2,2′-bipyridine complex.[3] Tris-(2-pyridinal-methylimine)-iron(II) has been shown to be diamagnetic. The stability of this structure indicates that there is a good chance of isolating the predicted optical and geometric isomers.

The cobalt(II) complex of 2-pyridinal-methylimine is quite different from the iron complex.

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[11] Value obtained from the weight of the residue after ignition.

[12] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

[13] Ref. 12, p. 92.

By analogy to the tris-(2,2′-bipyridine)-cobalt(II) complex,[1] oxidation should be accomplished quite easily. In order to obtain the pure cobalt(II) complex, the reaction was carried out in the absence of oxygen. The magnetic moment of 4.39 B.M. is somewhat more than the theoretical value for the spin-only moment for three unpaired electrons (3.87 B.M.).

In many respects, the nickel(II) complex of 2-pyridinal-methylimine is intermediate in character as compared to the iron(II) and cobalt(II) complexes. Oxidation of the nickel(II) is quite unlikely and, in this respect, the stability of the divalent complex resembles the iron(II) complex. The magnetic moment of 3.12 B.M. is comparable to that observed in other nickel(II) complexes (2.9 to 3.4 B.M.)[14] and indicates the spin-free regular octahedral structure. Since the nickel(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline have been resolved,[15] it seems quite likely that the optical isomers of the tris-(2-pyridinal-methylimine)-nickel(II) complex might be stable enough to permit resolution.

Complexes of 2,6-Pyridindial-bis-methylimine.—Since 2,6-pyridindial-bis-methylimine (PdMI) contains the same types of functional groups, this molecule would be expected to function as a chelating agent in a manner analogous to 2-pyridinal-methylimine, except that only two molecules are required to occupy the six positions of an octahedral complex ion. The free ligand is a white crystalline material melting at 23°; however, no polymerization was observed (as in the case of PMI). The boiling point is quite high (94° (3 mm.)). The ligand is soluble in water and alcohol but cannot be recrystallized from these solvents. It reacts with acetone to form a black glassy insoluble polymer which shows no evidence of complexing with metal ions. All of the complexes can be prepared with either the previously isolated ligand or by generation of the ligand *in situ.* Due to the decomposition of the ligand during distillation and the resulting low yields, the direct method is preferred.

The iron(II) complex was formed, in a straightforward manner, starting with the dialdehyde and methylamine. The complex produces the characteristic permanganate colored solutions, similar to those observed for iron(II) complexes of the dimethine class. It forms flat, black, shiny crystals. The complex was found to be diamagnetic; however, when corrections were made for the diamagnetic susceptibilities of the anion, ligand and water of hydration, the iron(II) atom was found to be slightly paramagnetic. The value of 0.71 Bohr magneton is in line with values found for other complexes of this type.[16]

The cobalt complex was first prepared from the free ligand and later by the alternative procedure. The magnetic moment of 2.31 Bohr magnetons for bis-(2,6-pyridindial-bis-methylimine)-cobalt(II) iodide is unusual.

The nickel(II) complex was prepared from the dialdehyde and methylamine and isolated as an orange-tan, crystalline product. The magnetic moment of the bis-(2,6-pyridindial-bis-methylmine)-nickel(II) iodide is 3.22 Bohr magnetonis indicating the usual spin-free octahedral structure.

Complexes of Biacetyl-bis-methylimine.—The compound biacetyl-bis-methylimine represents an extreme structure among the dimethine chelating agents. The series of complexes formed by this ligand is especially interesting since there are no aromatic rings present to mask the effects of coordination. However, the absence of aromatic rings and the associated resonance stabilization is accompanied by instability of the free ligand. The preparation of the free ligand has not been reported in the literature, and attempts to prepare it during the course of this investigation were unsuccessful. However the complexes form readily in aqueous solutions when biacetyl and methylamine are combined in the presence of a metal ion, such as iron(II), cobalt(II) or nickel(II).

The iron(II) complex was first prepared by Krumholz[1] and, in solution, exhibits the permanganate color characteristic of the iron(II) complexes of the dimethine class. The spectra and magnetic moment of the tris-(biacetyl-bis-methylimine)-iron(II) complex have been investigated[1,3,4] and indicate spin-pairing and an extreme electronic structure.

The cobalt(II) complex of biacetyl-bis-methylimine was isolated, with some difficulty, as the iodide salt. The solutions formed during the preparation of this substance tend to form a black tar which makes manipulations extremely difficult. The magnetic moment of 2.98 B.M. is quite close to that expected for two unpaired electrons. However, the cobalt(II) ion contains an odd number of electrons and its normal electronic configurations involve either one or three unpaired electrons.

The nickel(II) complex of biacetyl-bis-methylimine was found to be much easier to prepare than the cobalt(II) complex. The solution becomes dark red as soon as biacetyl and methylamine are combined in the presence of nickel(II) ions. The chloride salt is quite soluble, but the iodide salt is precipitated when excess iodide is added and the solution cooled. The magnetic moment of tris-(biacetyl-bis-methylimine)-nickel(II) iodide was found to be 3.24 Bohr magnetons, a value in close agreement with the nickel(II) complexes of 2-pyridinal-methylimine and 2,6-pyridindial-bis-methylimine.

Discussion

The usual electronic configuration for the d^6 ion, Fe^{2+}, in its solid *salts* and its normal complex compounds may be characterized as spin-free, having four unpaired electrons. It is true, however, that a few very well known complexes of iron(II) exhibit magnetic moments corresponding to no unpaired electrons. Examples of the most familiar of these are $[Fe(CN)_6]^{4-}$ and $[Fe(o\text{-phen})_3]^{2+}$. In keeping with the concepts of ligand field theory,[17] spin-pairing will occur only when the extra crystal field stabilization energy (20*D*q) exceeds the energy

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(14) Reference 12, p. 159.

(15) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales,* **83,** 263 (1950).

(16) R. C. Stoufer, Thesis, Ohio State University, 1958.

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 2; L. E. Orgel and J. S. Griffith, *Quart. Revs.*, **11**, 381 (1957).

required to pair the electrons (pairing energy). Although the values of these parameters are such that spin-pairing is expected in the case of ferrocyanide, the same is not true of tris-(*o*-phenanthroline)-iron(II).[18] The considerations mentioned here, when translated into the terminology of modern molecular orbital theory, are restricted to the sigma-bonding system of electrons, the t_{2g} levels (3-fold degenerate) being regarded as nonbonding. As has been suggested by a number of investigators, the unusual properties of these complexes may be explained on the assumption that the central metal ion and the ligand are linked by pi-bonds as well as by sigma-bonds, and it is the t_{2g} orbitals which should combine with ligand orbitals to produce the molecular orbitals of pi-symmetry. In the event such an interaction occurs, the bonding t_{2g} level will be lowered in energy and, consequently, the separation of t_{2g} from e_g will necessarily increase. This, in turn, must result in enhancement of the extra crystal field stabilization energy (c.f.s.e.) and, in view of the experimental facts (the complex is spin-paired), this extra c.f.s.e. must now exceed the pairing energy.

Similar arguments may be made for the bonding of ligands of the dipyridyl or *o*-phenanthroline class with cobalt(II) or nickel(II). However, the fact that these are d^7 and d^8 ions, respectively, results in some of the electrons populating the antibonding e_g^* energy level even in the spin-paired case. The symmetrical filling of both the e_g^* (half filled) and t_{2g} (filled) levels in nickel(II) leads to the prediction that this ion must always be spin-free and regular octahedral when it has a coördination number of six. In the case of cobalt(II) the spin-free complex has three unpaired electrons and a slight Jahn–Teller distortion[17] may arise from the orbital degeneracy of the t_{2g} level. The spin-paired cobalt(II) complex (one unpaired electron) should suffer measurable tetragonal distortion. As a first approximation, the regular octahedral structure may be assumed for both spin states. In this case the stable state is determined by the same considerations mentioned for iron(II). Again, pi-bond formation should favor the formation of the spin-paired state.

It should be pointed out that whereas the iron(II) and nickel(II) complexes with PMI, PdMI and BMI conform closely in magnetic behavior (Table II) to the pattern familiar in similar, well-known compounds (as described above), the corresponding cobalt(II) complexes exhibit an unusual behavior shared with only a few other compounds. The magnetic moment of $[Co(PMI)_3](BF_4)_2$, 4.39 Bohr magnetons, is substantially higher than that expected for three unpaired electrons (3.87 Bohr magnetons). However, this behavior has been noted[14] in other cobalt(II) complexes (observed range 4.4–5.2) and is generally attributed to incomplete quenching of the orbital contribution to the magnetic moment.[19] In fact, Nyholm[20] has pointed out that a value of approximately 4.8 to 5.2 Bohr magnetons is commonly observed for spin-free, octahedral cobalt(II). On that basis, the observed moment is deemed to be somewhat lower than the most probable value. Further, Nyholm has related moments substantially below 5 Bohr magnetons to tetrahedral structures. Because of the presence of three moles of a bidentate ligand in the complex ion $[Co(PMI)_3]^{++}$, a tetrahedral structure is discounted. By comparison, the moments for $[Co(BMI)_3]I_2 \cdot H_2O$ and $[Co(PdMI)_2]I_2 \cdot H_2O$ are much lower than the usual spin-free values. The value of 2.98 Bohr magnetons for $[Co(BMI)_3]I_2 \cdot H_2O$ is quite close to that expected for two unpaired electrons. However, the cobalt(II) ion contains an odd number of electrons and its normal electronic configurations involve one or three electrons. Similarly, the magnetic moment of $[Co(PdMI)_2]I_2 \cdot H_2O$, 2.31 Bohr magnetons, is abnormally high for one unpaired electron. The observed moments can be explained by assuming an equilibrium mixture of the spin-paired (inner orbital) and spin-free (outer orbital) states in each case. From this, it is concluded that the metal–ligand bonds must be quite strong, involving appreciable pi-bonding and that the energy difference between the two electronic states (spin-paired and spin-free) is of the order of kT.

According to modern ligand field and molecular orbital theories, the formation of spin-paired octahedral cobalt(II) should be only a few kcal. less favorable than spin-paired iron(II). In this particular case, the older valence bond theory makes the absurd prediction that spin-paired octahedral cobalt(II) complexes are some 580 kcal./mole less stable than the analogous iron(II) complexes.[21] However, well established examples of spin-paired, octahedral cobalt(II) complexes are extremely rare. In fact, most of them have been prepared only recently. In addition to the compounds reported here, these others are likely examples: hexanitrocobaltate(II),[22] tris-(*o*-phenylene-bis-dimethylarsine)-cobalt(II),[23] bis-(2,6-pyridindial-dihydrazone)-cobalt(II),[8] bis-(2,6-pyridindial-bis-benzylimine)-cobalt(II)[9] and (3,6-dithiaoctan-1,8-dial-bis-α-pyridylhydrazone)-cobalt(II).[24] It is probably significant that three of the seven examples of spin-paired, octahedral cobalt(II) compounds involve tridentate, unsaturated nitrogen donors. $Co(BMI)_3I_2 \cdot H_2O$ appears to be the first example of a spin-paired octahedral cobalt(II) complex containing bidentate ligands of this class: *i.e.*, the cobalt(II) complexes of *o*-phenanthroline, 2,2′-bipyridine, etc., are spin-free.

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(19) Reference 12, p. 170.

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(21) D. H. Busch, *J. Chem. Ed.*, **33**, 376 (1956).

(22) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 116.

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