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Transition Metal Complexes with Ligands Derived from 2-Sulfenamidopyridine

BY MARTIN A. ROBINSON AND THOMAS J. HURLEY

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A variety of complexes have been synthesized with ligands derived from the Schiff base reaction of 2-pyridinaldehyde and 2-acetylpyridine with 2-sulfenamidopyridine, 2-sulfenamido-4-methylpyridine, and 2-sulfenamidopyridine 1-oxide. The resultant ligands all chelate in a tridentate manner. Magnetic moments, molar conductances, and spectral data have been applied to the characterization of the complexes. The properties of the cobalt(II) and nickel(II) species are typical of spin-free octahedral structures in all cases. In contrast, the iron(II) complexes show significant changes in properties coinciding with alterations in the structures of the ligands. All the Schiff base ligands derived from 2-sulfenamidopyridine and 2-sulfenamido-4-methylpyridine result in iron(II) complexes which are diamagnetic, a behavior which is typical for imines of this type. In contrast is the behavior of bis((N-(2-thiopyridine 1-oxide)2-pyridinalimine))iron(II) perchlorate, which is paramagnetic with a moment of 5.16 B.M. Finally, a study of the visible spectra of the nickel complexes of the various ligands suggests that the electron pair on the sulfur atom of the sulfenamide moiety is not appreciably delocalized.

Introduction

Since the turn of the century when Blau[1] first reported on 2,2′-bipyridine, a great deal of interest has centered on ligands containing the α-diimine linkage (–N=C—C=N–). Of particular fascination has been the nature of the metal–nitrogen bond in the metal chelates. The interest has been aroused because of the unusual stability of these complexes as demonstrated by the diamagnetism exhibited by almost all iron(II) complexes containing this array of atoms. This typical behavior has been reported for the iron(II) complexes of pyridinalimines,[2] α-diketodihydrazones,[3] pyridinalhydrazones,[4] and so forth. An exception is tris(2-pyridinaldimethylhydrazone)iron(II) iodide which has a magnetic moment of 5.45 B.M.[5] This anomalous behavior is a consequence of steric considerations which results in a forced lengthening of the metal–nitrogen bond.

The research reported herein is concerned with the synthesis of a new group of ligands containing the α-diimine array as well as the preparation and characterization of 28 transition metal derivatives.

Experimental

Materials.—2-Pyridinaldehyde and 2-acetylpyridine were obtained from Aldrich Chemical Co. and purified when necessary. Sodium 2-thiopyridine 1-oxide was obtained from the Olin Mathieson Chemical Corp. All the metal perchlorates were purchased from the G. F. Smith Co. and used without further purification. The other materials are standard reagent grade chemicals.

Complexes of 2-Sulfenamidopyridine. 2-Mercaptopyridine.—This compound was synthesized by the method of Thirtle[6]; m.p. 126–128°. *Anal.* Calcd. for C_5H_5NS: C, 54.1; H, 4.5; N, 12.6. Found: C, 54.1; H, 4.5; N, 12.5.

2-Sulfenamidopyridine.—An aqueous chloramine solution was prepared by the slow addition of 90 ml. of an iced 1.84 *M* sodium hypochlorite solution to 278 ml. of a 1.84 *M* ammonium hydroxide solution which had been previously cooled to $-5°$. To the resulting chloramine solution, an aqueous solution of the sodium salt of 2-mercaptopyridine (16.5 g., 0.15 mole) was added slowly, taking care that the temperature did not exceed 5°. The desired product precipitated immediately and was filtered, vacuum dried to remove excess water, and recrystallized from a petroleum ether–isopropyl alcohol mixture. This resulted in 10.5 g. (55% yield) of a white crystalline product; m.p. 79–80°. *Anal.* Calcd. for $C_5H_6N_2S$: C, 47.6; H, 4.8; N, 22.2. Found: C, 47.7; H, 5.2; N, 22.1.

Dichlorobis(2-sulfenamidopyridine)iron(II) 1-Hydrate.—Ferrous chloride 4-hydrate (2.0 g., 0.01 mole) was dissolved in methanol and added dropwise, with stirring, to a methanol solution of 2-sulfenamidopyridine (3.8 g., 0.03 mole). The mixture was stirred for an additional 30 min. and then placed in a refrigerator overnight. The brown solid that formed was filtered, washed successively with methanol and ether, and air dried; yield 45%. *Anal.* Calcd. for $[Fe(C_5H_6N_2S)_2Cl_2] \cdot H_2O$: C, 30.2; H, 3.5; N, 14.1; Fe, 14.1. Found: C, 29.8; H, 3.7; N, 14.0; Fe, 14.5.

Dichlorobis(2-sulfenamidopyridine)cobalt(II).—This compound was isolated as a pink material in a method analogous to that previously described; yield 30%. *Anal.* Calcd. for $[Co(C_5H_6N_2S)_2Cl_2]$: C, 31.4; H, 3.1; N, 14.7; Co, 15.4. Found: C, 31.7; H, 3.2; N, 14.7; Co, 15.0.

Tris(2-sulfenamidopyridine)iron(II) Perchlorate.—Ferrous perchlorate 6-hydrate (1.2 g., 0.0033 mole) was dissolved in methanol and added dropwise, with stirring, to a methanol

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(1) F. Blau, *Ber.*, **21**, 1007 (1888).

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(3) R. C. Stoufer and D. H. Busch, *ibid.*, **78**, 6016 (1956).

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(5) M. A. Robinson, J. N. Curry, and D. H. Busch, *ibid.*, **2**, 1178 (1963).

(6) J. R. Thirtle, *J. Am. Chem. Soc.*, **68**, 342 (1946).

solution of 2-sulfenamidopyridine (1.3 g., 0.011 mole). After a short period of time, aqua crystals precipitated. They were filtered, washed with methanol and then ether, and dried *in vacuo* over P_2O_5 at 100°; yield 90%. *Anal.* Calcd. for $[Fe(C_5H_6N_2S)_3](ClO_4)_2$: C, 28.4; H, 2.8; N, 13.3; Fe, 8.8. Found: C, 28.0; H, 2.5; N, 13.1; Fe, 8.6.

Tris(2-sulfenamidopyridine)cobalt(II) Perchlorate.—In a manner similar to that previously described for the iron(II) analog, this complex was isolated as a brown solid; yield 60%. *Anal.* Calcd. for $[Co(C_5H_6N_2S)_3](ClO_4)_2$: C, 28.3; H, 2.8; N, 13.2; Co, 9.3. Found: C, 28.4; H, 2.7; N, 13.2; Co, 9.5.

Complexes of N(2-Thiopyridine)2-pyridinalimine. N(2-Thiopyridine)2-pyridinalimine.—2-Sulfenamidopyridine (2.4 g., 0.19 mole) was dissolved in 15 ml. of methanol. To this solution, 2.0 g. of 2-pyridinaldehyde (0.17 mole) was added slowly with stirring. The solution was held at reflux for 1.5 hr. and the methanol was removed by means of a rotary evaporator. A yellow oil remained. The product was mixed with a carbon tetrachloride–petroleum ether solution, and upon the addition of a small quantity of ether, yellow crystals formed; m.p. 90–93°. *Anal.* Calcd. for $C_{11}H_9N_3S$: C, 61.4; H, 4.2; N, 19.5. Found: C, 61.7; H, 4.4; N, 19.8.

Bis((N(2-thiopyridine)2-pyridinalimine))iron(II) Perchlorate 1-Hydrate.—Iron perchlorate 6-hydrate (0.80 g., 0.0022 mole) was dissolved in 20 ml. of methanol. This was added slowly, with stirring, to 1.4 g. (0.0066 mole) of N(2-thiopyridine)2-pyridinalimine which had been dissolved in a water–methanol solution. The solution was stirred for an additional 15 min. and placed in a refrigerator overnight. The purple crystals that formed were filtered, washed with methanol and ether, and dried *in vacuo* over P_2O_5 at 60°; yield 67%. *Anal.* Calcd. for $[Fe(C_{11}H_9N_3S)_2](ClO_4)_2\cdot H_2O$: C, 37.6; H, 2.8; N, 12.0; Fe, 8.0. Found: C, 37.5; H, 2.9; N, 12.0; Fe, 7.7.

Bis((N(2-thiopyridine)pyridinalimine))cobalt(II) Perchlorate 1-Hydrate.—This compound was prepared as orange crystals in a manner analogous to that reported for the iron(II) complex; yield 94%. *Anal.* Calcd. for $[Co(C_{11}H_9N_3S)_2](ClO_4)_2\cdot H_2O$: C, 37.4; H, 2.8; N, 11.9; Co, 8.4. Found: C, 37.7; H, 3.1; N, 11.9; Co, 8.5.

Bis((N(2-thiopyridine))2-pyridinalimine)nickel(II) Perchlorate 1.5-Hydrate.—This compound was obtained as tan crystals in the aforementioned manner; yield 78%. *Anal.* Calcd. for $[Ni(C_{11}H_9N_3S)_2](ClO_4)_2\cdot 1.5H_2O$: C, 36.9; H, 2.9; N, 11.7; Ni, 8.3. Found: C, 37.2; H, 2.8: N, 11.7; Ni, 8.6.

Bis((N(2-thiopyridine)2-pyridinalimine))copper(II) Perchlorate.—In a manner analogous to that previously described for the iron(II) complex, but utilizing a 2:1 ligand–metal ratio, this compound was obtained as a brown solid; yield 95%. *Anal.* Calcd. for $[Cu(C_{11}H_9N_3S)_2](ClO_4)_2$: C, 38.1; H, 2.6; N, 12.1; Cu, 9.2. Found: C, 37.7; H, 2.6; N, 12.1; Cu, 8.8.

Bis((N(2-thiopyridine)2-pyridinalimine)zinc(II) Perchlorate 2-Hydrate.—Using a 2:1 ligand–metal ratio, this compound was isolated as a yellow solid; yield 85%. *Anal.* Calcd. for $[Zn(C_{11}H_9N_3S)_2](ClO_4)_2\cdot 2H_2O$: C, 36.2; H, 3.0; N, 11.5; Zn, 8.9. Found: C, 35.9; H, 3.0: N, 11.5; Zn, 9.2.

Complexes of N(2-Thiopyridine)2-acetylpyridineimine. Bis((N(2-thiopyridine)2-acetylpyridineimine))cobalt(II) Perchlorate.—Cobalt perchlorate 6-hydrate (3.7 g., 0.01 mole) was dissolved in 50 ml. of methanol and added quickly to a solution of 3.8 g. (0.03 mole) of 2-sulfenamidopyridine in 150 ml. of methanol. To this solution 3.7 g. (0.031 mole) of 2-acetylpyridine was added quickly and the solution was heated to relux and stirred for 30 min. The orange precipitate that formed was filtered, recrystallized from methanol, and dried for 24 hr. *in vacuo* over P_2O_5 at 100°; yield 88%. *Anal.* Calcd. for $[Co(C_{12}H_{11}N_3S)_2](ClO_4)_2$: C, 40.2; H, 3.1; N, 11.7; Co, 8.2. Found: C, 40.3; H, 3.2; N, 11.9; Co, 8.1. Alternatively, the cobalt perchlorate 6-hydrate can be mixed with 2-acetylpyridine and then allowed to react with 2-sulfenamidopyridine. The final product is the same.

Bis((N(2-thiopyridine)2-acetylpyridineimine))nickel(II) Perchlorate.—In a manner analogous to that previously described for the cobalt(II) complex, this compound was isolated as tan crystals; yield 90%. *Anal.* Calcd. for $[Ni(C_{12}H_{11}N_3S)_2](ClO_4)_2$: C, 40.2; H, 3.1; N, 11.7; Ni, 8.2. Found: C, 40.1; H, 3.1; N, 12.0; Ni, 8.0.

Bis((N(2-thiopyridine)2-acetylpyridineimine))zinc(II) Perchlorate.—In the same manner as that described above, this complex was isolated as a white solid; yield 75%. *Anal.* Calcd. for $[Zn(C_{12}H_{11}N_3S)_2](ClO_4)_2$: C, 39.9; H, 3.1; N , 11.6; Zn, 9.0. Found: C, 39.5; H, 3.0; N, 11.8; Zn, 8.9.

Bis((N(2-thiopyridine)2-acetylpyridineimine))iron(II) Perchlorate.—Since the complex formed between iron(II) perchlorate and 2-sulfenamidopyridine is so insoluble, special purification methods were necessary to obtain the desired complex. The compound was obtained in highest yields by mixing the methanol solution of iron(II) chloride 4-hydrate with 2-acetylpyridine and then adding the methanol solution of 2-sulfenamidopyridine dropwise, with stirring. The solution was held at reflux for 10 min. and then a 100% excess of sodium perchlorate dissolved in methanol was added. The solid that formed was still impure. Purification was obtained by placing the solid in water. The desired compound was soluble and was isolated as a purple solid after removal of the water, washing with a mixture of ethanol and ether, and then ether alone, and drying *in vacuo* over P_2O_5 at 100°; yield 25%. *Anal.* Calcd. for $[Fe(C_{12}H_{11}N_3S)_2](ClO_4)_2\cdot 3H_2O$: C, 37.5; H, 3.6; N, 10.9; Fe, 7.3. Found: C, 37.1; H, 3.1; N, 10.5; Fe, 7.2.

Complexes of N(2-Thiopyridine 1-oxide)2-pyridinalimine. 2-Sulfenamidopyridine 1-Oxide.—Sodium 2-thiopyridine 1-oxide (40.0 g., 0.268 mole) was dissolved in 100 ml. of water. This solution was added slowly, with stirring, to a freshly prepared chloramine solution (made from 156 ml. of 2.12 *M* sodium hypochlorite and 556 ml. of 1.84 *M* ammonium hydroxide). The reaction mixture was not permitted to rise above 0°. Shortly after completion of the addition, a white solid formed which was filtered and recrystallized from methanol; yield 55%; m.p. 147–149° dec. *Anal.* Calcd. for C_5H_6NOS: C, 42.3; H, 4.2; N, 19.7. Found: C, 42.2; H, 4.5; N, 19.9.

N(2-Thiopyridine 1-oxide)2-pyridinalimine.—2-Sulfenamidopyridine 1-oxide (6.0 g., 0.04 mole) was dissolved in methanol. 2-Pyridinaldehyde (5.4 g., 0.050 mole) was added dropwise, with stirring, and the reaction mixture was held at reflux for 18 hr. The solution was cooled and the methanol was removed on a rotary evaporator. The yellow solid that remained was recrystallized from a 90:10 ether–methanol mixture. The white crystals that formed melted at 107–110°; yield 60%. *Anal.* Calcd. for $C_{11}H_9N_3OS$: C, 57.1; H, 3.9; N, 18.2. Found: C, 57.2; H, 3.9; N, 18.2.

Bis((N(2-thiopyridine 1-oxide)2-pyridinalimine))cobalt(II) Perchlorate.—Cobalt perchlorate 6-hydrate (0.7 g., 0.0019 mole) was dissolved in methanol and added dropwise, with stirring, to a methanol solution of 2-pyridinal-N(2-thiopyridine 1-oxide)imine (1.0 g., 0.0043 mole). An orange precipitate formed which was filtered under nitrogen, washed extensively with ether, and dried under nitrogen. Once this complex is dried, it is stable in air; yield 85%. *Anal.* Calcd. for $[Co(C_{11}H_9N_3OS)_2](ClO_4)_2$: C, 36.7; H, 2.5; N, 11.7; Co, 8.2. Found: C, 36.3; H, 2.5; N, 11.9; Co, 8.2.

Bis((N(2-thiopyridine 1-oxide)2-pyridinalimine))nickel(III) Perchlorate.—This compound was isolated as brown crystals in a manner analogous to that previously described for the cobalt compound: yield 88%. *Anal.* Calcd. for $[Ni(C_{11}H_9N_3OS)_2](ClO_4)_2$: C, 36.7; H, 2.5; N, 11.7; Ni, 8.2. Found: C, 36.7; H, 2.6; N, 11.8; Ni, 7.9.

Bis((N(2-thiopyridine 1-oxide)2-pyridinalimine))iron(II) Perchlorate 1-Hydrate.—The reaction was conducted in the same manner as that previously described. However, no solid precipitated out. Therefore, anhydrous ether was added to the reaction mixture until a blue precipitate formed which was then treated as with the analogous complexes; yield 96%. *Anal.* Calcd. for $[Fe(C_{11}H_9N_3OS]_2](ClO_4)_2\cdot H_2O$: C, 35.9; H, 2.7; N, 11.4; Fe, 7.6. Found: C, 36.1; H, 3.1; N, 11.2; Fe, 7.2.

Complexes of N(2-Thio-4-methylpyridine)2-pyridinalimine.

2-Sulfenamido-4-methylpyridine.—In a manner analogous to that described for the preparation of 2-sulfenamidopyridine, and starting with 2-mercapto-4-methylpyridine, the desired compound was isolated as a white solid. It was recrystallized out of a mixture of petroleum ether and benzene; yield 50%. *Anal.* Calcd. for $C_6H_8N_2S$: C, 51.4; H, 5.7; N, 20.0. Found: C, 51.3; H, 5.8; N, 20.1.

Bis((N(2-thio-4-methylpyridine)2-pyridinalimine))cobalt(II) Perchlorate.—Cobalt(II) perchlorate 6-hydrate (1.3 g., 0.0033 mole) was dissolved in methanol and added quickly to 2-pyridinaldehyde (1.1 g., 0.01 mole). The mixture was warmed and added slowly to a methanol solution of 2-sulfenamido-4-methylpyridine (1.4 g., 0.01 mole). A precipitate formed immediately. The solution was heated to reflux for 5 min. and allowed to stand in a refrigerator overnight. The brown solid was filtered, recrystallized from methanol, washed with ether, and air dried; yield 90%. *Anal.* Calcd. for $[Co(C_{12}H_{11}N_3S)_2](ClO_4)_2$: C, 40.2; H, 3.1; N, 11.7; Co, 8.2. Found: C, 40.4; H, 3.0; N, 11.6; Co, 8.1.

Bis((N(2-thio-4-methylpyridine)2-pyridinalimine))iron(II) Perchlorate.—In a manner similar to that previously described, this compound was isolated as a purple solid; yield 80%. *Anal.* Calcd. for $[Fe(C_{12}H_{11}N_3S)_2](ClO_4)_2$: C, 40.4; H, 3.1; N, 11.8; Fe, 7.9. Found: C, 40.7; H, 3.4; N, 11.8; Fe, 7.8.

Complexes of N(2-Thio-4-methylpyridine)2-acetylpyridineimine. Bis((N(2-thio-4-methylpyridine)2-acetylpyridineimine))-cobalt(II) Perchlorate.—Cobalt(II) perchlorate 6-hydrate (1.3 g., 0.0036 mole) was dissolved in 50 ml. of methanol and added quickly to 2-acetylpyridine (1.2 g., 0.01 mole). The solution was held at reflux for 15 min. and then added slowly, with stirring, to a methanol solution of 2-sulfenamido-4-methylpyridine (1.4 g., 0.01 mole). The solution was stirred for an additional 15 min. and placed in a refrigerator overnight. The orange solid that formed was filtered, washed with ether, recrystallized from ethanol, and dried *in vacuo* over P_2O_5 at 100°; yield 76%. *Anal.* Calcd. for $[Co(C_{13}H_{13}N_3S)_2](ClO_4)_2$: C, 41.9; H, 3.5; N, 11.3; Co, 7.9. Found: C, 42.0; H, 3.8; N, 11.3; Co, 7.7.

Bis((N(2-thio-4-methylpyridine)2-acetylpyridineimine))nickel-(II) Perchlorate.—This compound was prepared in a manner similar to that previously described for the analogous cobalt compound. The complex was isolated as tan crystals; yield 80%. *Anal.* Calcd. for $[Ni(C_{13}H_{13}N_3S)_2](ClO_4)_2$: C, 41.9; H, 3.5; N, 11.3; Ni, 7.9. Found: C, 41.8; H, 3.6; N, 11.2; Ni, 7.9.

Bis((N(2-thio-4-methylpyridine)2-acetylpyridineimine))iron(II) Perchlorate 2-Hydrate.—This compound was prepared in essentially the same manner as that previously described. However, the purification was somewhat different. After the complex had formed, it was filtered and washed with ethanol and ether. It was then dissolved in distilled water. The water was removed and the remaining purple solid was washed with an ether–methanol mixture and then ether alone. It was dried *in vacuo* over P_2O_5 at 100°; yield 40%. *Anal.* Calcd. for $[Fe(C_{13}H_{13}N_3S)_2](ClO_4)_2 \cdot 2H_2O$: C, 40.1; H, 3.9; N, 10.8; Fe, 7.2. Found: C, 39.8; H, 3.8; N, 11.0; Fe, 6.8.

Complexes of N-Ethylidene-2-sulfenamidopyridine. N-Ethylidene-2-sulfenamidopyridine.—2-Sulfenamidopyridine (12.6 g., 0.10 mole) was dissolved in absolute methanol. Freshly distilled acetaldehyde (4.8 g., 0.11 mole) was added slowly with stirring. After addition, the solution was stirred for an additional 30 min. and fractionated, and the material was collected as an oil; b.p. 106–108° (3 mm.). *Anal.* Calcd. for $C_7H_8N_2S$: C, 55.3; H, 5.3; N, 18.4. Found: C, 55.2; H, 5.3; N, 18.4.

Tris(N-ethylidene-2-sulfenamidopyridine)cobalt(II) Perchlorate.—Cobalt(II) perchlorate 6-hydrate (3.6 g., 0.01 mole) was dissolved in absolute methanol and added dropwise, with stirring, to a solution of N-ethylidene-2-sulfenamidopyridine (4.5 g., 0.03 mole) in 50 ml. of methanol. A brown precipitate formed which was washed successively with water, methanol, and ether and dried under vacuum at 100°; yield 85%. *Anal.* Calcd. for $[Co(C_7H_8N_2S)_3](ClO_4)_2$: C, 35.3; H, 3.4; N, 11.8; Co, 8.3. Found: C, 35.3; H, 3.3; N, 11.8; Co, 8.5.

Tris(N-ethylidene-2-sulfenamidopyridine)nickel(II) Perchlorate.—In a manner analogous to that described for the cobalt compound, this complex was isolated as a lavender solid; yield 90%. *Anal.* Calcd. for $[Ni(C_7H_8N_2S)_3](ClO_4)_2$: C, 35.3; H, 3.4; N, 11.8; Ni, 8.3. Found: C, 34.9; H, 3.3; N, 12.1; Ni, 8.1.

Complexes of N-Propylidene-2-sulfenamidopyridine. N-Propylidene-2-sulfenamidopyridine.—2-Sulfenamidopyridine (12.6 g., 0.10 mole) was dissolved in absolute methanol. Freshly distilled propionaldehyde (6.4 g., 0.11 mole) was added slowly with stirring. The solution was refluxed for an additional 30 min. and fractionated, and the material was collected as an oil; b.p. 115–116° (3.5 mm.). *Anal.* Calcd. for $C_8H_{10}N_2S$: C, 57.8; H, 6.0; N, 16.9. Found: C, 57.5; H, 6.2; N, 16.4.

Tris(N-propylidene-2-sulfenamidopyridine)cobalt(II) Perchlorate 1-Hydrate.—Cobalt perchlorate 6-hydrate (3.6 g., 0.01 mole) was dissolved in absolute methanol and added dropwise, with stirring, to a solution of N-propylidene-2-sulfenamidopyridine (5.0 g., 0.03 mole) in 50 ml. of absolute methanol. A yellow precipitate formed which was filtered, washed successively with water, methanol, and ether; and dried under vacuum at 100° yield 90%. *Anal.* Calcd. for $[Co(C_8H_{10}N_2S)_3](ClO_4)_2 \cdot H_2O$: C, 37.2; H, 4.1; N, 10.9; Co, 7.6. Found: C, 36.9; H, 3.9; N, 11.1; Co, 7.4.

Tris(N-propylidene-2-sulfenamidopyridine)nickel(II) Perchlorate 2-Hydrate.—In a manner similar to that described for the cobalt(II) analog, this complex was isolated as a lavender solid; yield 90%. *Anal.* Calcd. for $[Ni(C_8H_{10}N_2S)_3](ClO_4)_2 \cdot 2H_2O$: C, 36.3; H, 4.3; N, 10.6; Ni, 7.4. Found: C, 36.0; H, 3.9; N, 10.7; Ni, 7.4.

Complexes of N-*n*-Butylidene-2-sulfenamidopyridine. N *n*-Butylidene-2-sulfenamidopyridine.—2-Sulfenamidopyridine (12.6 g., 0.10 mole) was dissolved in absolute methanol. Freshly distilled butyraldehyde (7.9 g., 0.11 mole) was added slowly, with stirring. The solution was brought to reflux and held there for an additional 30 min. and fractionated, and the desired material was collected as an oil; b.p. 128–131° (4 mm.). *Anal.* Calcd. for $C_9H_{12}N_2S$: C, 60.0; H, 6.7; N, 15.6. Found: C, 60.1; H, 6.8; N, 15.6.

Tris(N-*n*-butylidene-2-sulfenamidopyridine)cobalt(II) Perchlorate.—Cobalt perchlorate 6-hydrate (3.6 g., 0.01 mole) was dissolved in absolute methanol and added, with stirring, to a solution of N-*n*-butylidene-2-sulfenamidopyridine (5.4 g., 0.03 mole) in 50 ml. of absolute methanol. A yellow precipitate formed which was filtered, washed successively with water, methanol, and ether, and dried under vacuum at 100°; yield 88%. *Anal.* Calcd. for $[Co(C_9H_{12}N_2S)_3](ClO_4)_2$: C, 40.6; H, 4.5; N, 10.5; Co, 7.4. Found: C, 40.4; H, 4.4; N, 11.0; Co, 7.5.

Tris(N-*n*-butylidene-2-sulfenamidopyridine)nickel(II) Perchlorate.—This compound was isolated as a lavender material in a method analogous to that previously described for the cobalt(II) complex; yield 92%. *Anal.* Calcd. for $[Ni(C_9H_{12}N_2S)_3](ClO_4)_2$: C, 40.6; H, 4.5; N, 10.5; Ni, 7.4. Found: C, 40.6; H, 4.1; N, 10.6; Ni, 7.4.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities were obtained at room temperature by the Gouy method using ferrous ammonium sulfate 6-hydrate and nickel(II) chloride 6-hydrate as standards. Magnetic moment values were obtained by use of the spin-only formula. Diamagnetic corrections were made for the ligands and anions so that the reported values are the moments attributable to the metal ions (Table I).

Conductivity Measurements.—Molar conductances were measured using an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 0.500 cm.$^{-1}$. The measurements were made at 25° employing 10^{-3} *M* solutions and a bridge frequency of 1000 c.p.s. (Table I).

Spectra.—The spectra in the visible region were obtained by employing a Cary Model 14 recording spectrophotometer and matched cells with fused quartz windows. Methanol was used as the solvent. However, the spectral measurements for $Ni(ES)_2^{2+}$, $Ni(PS)_2^{2+}$, and $Ni(BS)_2^{2+}$ were obtained in dimethylformamide because of the insolubility of these ions in methanol. All measurements were made on 10^{-1} *M* solutions in 1-cm. cells.

TABLE I

PROPERTIES OF THE COMPLEXES

Complexes[a]	Color	Molar suscept.[b] $\times 10^{-6}$	Mag. moment,[b] B.M.	Molar conductivity,[c] ohm^{-1}/cm.
$Fe(SAP)_2Cl_2$	Brown	11,356.37	5.27	Insoluble
$Co(SAP)_2Cl_2$	Pink	9,628.18	4.86	233
$Fe(SAP)_3(ClO_4)_2$	Aqua	2,952.61	2.79	64[d]
$Co(SAP)_3(ClO_4)_2$	Brown	1,857.98	2.27	76[d]
$Fe(TPPI)_2(ClO_4)_2 \cdot H_2O$	Purple	Diamagnetic	~0	192
$Co(TPPI)_2(ClO_4)_2 \cdot H_2O$	Orange	8,479.08	4.60	217
$Ni(TPPI)_2(ClO_4)_2 \cdot 1.5H_2O$	Brown	3,745.56	3.13	192
$Cu(TPPI)_2(ClO_4)_2$	Brown	. . .	. . .	229
$Zn(TPPI)_2(ClO_4)_2 \cdot 2H_2O$	Yellow	. . .	. . .	230
$Fe(TPAPI)_2(ClO_4)_2 \cdot 3H_2O$	Purple	Diamagnetic	~0	330
$Co(TPAPI)_2(ClO_4)_2$	Orange	9,816.68	4.94	244
$Ni(TPAPI)_2(ClO_4)_2$	Tan	3,688.16	3.11	228
$Zn(TPAPI)_2(ClO_4)_2$	White	. . .	. . .	220
$Fe(TPOPI)_2(ClO_4)_2$	Blue	10,756.02	5.16	238
$Co(TPOPI)_2(ClO_4)_2$	Orange	10,542.59	5.11	250
$Ni(TPOPI)_2(ClO_4)_2$	Tan	3,885.55	3.18	256
$Fe(TMPPI)_2(ClO_4)_2$	Purple	Diamagnetic	~0	210
$Co(TMPPI)_2(ClO_4)_2$	Brown	9,249.23	4.80	200
$Ni(TMPPI)_2(ClO_4)_2$	Tan	4,112.72	3.27	200
$Fe(TMPAPI)_2(ClO_4)_2 \cdot 2H_2O$	Purple	Diamagnetic	~0	200
$Co(TMPAPI)_2(ClO_4)_2$	Orange	8,065.25	4.50	192
$Ni(TMPAPI)_2(ClO_4)_2$	Tan	3,847.43	3.18	200
$Co(ES)_3(ClO_4)_2$	Brown	9,286.44	4.81	161[d]
$Ni(ES)_3(ClO_4)_2$	Lavender	3,867.35	3.18	156[d]
$Co(PS)_3(ClO_4)_2 \cdot H_2O$	Yellow	9,438.12	4.86	143[d]
$Ni(PS)_3(ClO_4)_2 \cdot 2H_2O$	Lavender	4,297.70	3.18	147[d]
$Co(BS)_3(ClO_4)_2$	Yellow	8,088.60	4.52	147[d]
$Ni(BS)_3(ClO_4)_2$	Lavender	4,010.85	3.26	143[d]

[a] Abbreviations have been listed in another part of this paper. [b] Molar susceptibility values were obtained at 25° and are uncorrected. Reported magnetic moments are corrected for the diamagnetism of the ligands and anions. [c] Measurements were made on 10^{-3} M solutions employing water as the solvent medium except where cited. [d] Measurements were made on 10^{-3} M solutions in dimethylformamide.

TABLE II

ABSORPTION BANDS OF DIVALENT NICKEL COMPLEX IONS

Divalent complex ions[a]	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ cm.$^{-1}$	ϵ	$^3A_{2g} \rightarrow {}^1E_g$ cm.$^{-1}$	ϵ	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ cm.$^{-1}$	ϵ	Dq,[c] cm.$^{-1}$
$Ni(SAP)_3$	10,990	. . .	12,720	. . .	17,860	. . .	1099
$Ni(TPPI)_2$[b]	12,350	17	11,560	12	. . .	. . .	1235
$Ni(TPAPI)_2$[b]	12,500	28	11,450	22	20,830	34	1250
$Ni(TMPPI)_2$[b]	12,420	23	11,490	17	19,610	35	1242
$Ni(TMPAPI)_2$[b]	12,350	27	11,490	22	. . .	. . .	1235
$Ni(TPOPI)_2$	9,800	6	12,990	3	16,390	5	980
$Ni(ES)_3$	10,310	8	12,660	3	16,670	6	1031
$Ni(PS)_3$	10,200	8	12,282	2	16,390	5	1020
$Ni(BS)_3$	10,260	6	12,820	1	16,530	4	1026

[a] Abbreviations are presented elsewhere in this report. [b] In these complexes, the first two spectral band assignments could possibly be reversed. This is still a point of conjecture. [c] Dq values were obtained directly from the assigned $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ band.

All infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics. Potassium bromide pellets were utilized and the results were checked out by employing mulls of fluorolube and Nujol. (Table III).

TABLE III

SPECTRAL DATA (CM.$^{-1}$) FOR N(2-THIOPYRIDINE 1-OXIDE)2-PYRIDINALIMINE COMPLEXES

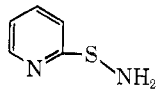
Compound	N–O str.	N–O bend
TPOPI	1230 s 1215 sh	845 s
$[Fe(TPOPI)_2](ClO_4)_2$	1210 s (wide)	838 s
$[Co(TPOPI)_2](ClO_4)_2$	1220 s 1200 s	833 s
$[Ni(TPOPI)_2](ClO_4)_2$	1215 m 1200 s	838 s

Abbreviations.—The following abbreviations will be employed throughout this publication: SAP, 2-sulfenamidopyridine; TPPI, N(2-thiopyridine)2-pyridinalimine; TPAPI, N(2-thiopyridine)2-acetylpyridineimine; TPOPI, N(2-thiopyridine 1-oxide)2-pyridinalimine; TMPPI, N(2-thio-4-methylpyridine)2-pyridinalimine; TMPAPI, N(2-thio-4-methylpyridine)2-acetylpyridineimine; ES, N-ethylidene-2-sulfenamidopyridine; PS, N-propylidene-2-sulfenamidopyridine; BS, N-*n*-butylidene-2-sulfenamidopyridine.

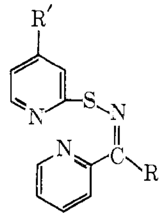
It should be noted that the various perchlorate complexes reported herein are quite explosive and should be handled with care.

Results and Discussion

Complexes of divalent iron, cobalt, nickel, and, in several instances, copper and zinc, have been prepared with several new ligands (I, II, III, IV), where R = H,



I



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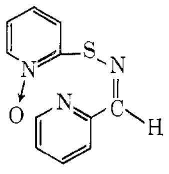
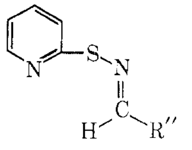


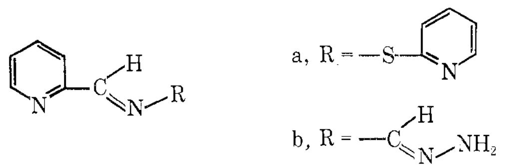
III



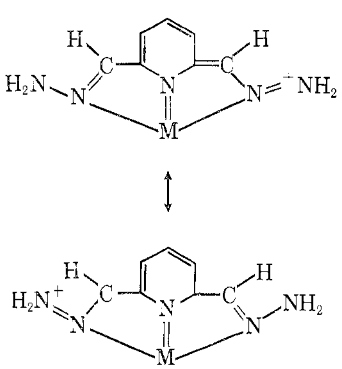
IV

CH_3; R′ = H, CH_3; R″ = CH_3, C_2H_5, C_3H_7. Two types of complexes have been isolated from the reaction of 2-sulfenamidopyridine (I) with divalent cobalt and iron. They are of the general formulas $[ML_2X_2]$ and $[ML_3]X_2$, where L is a bidentate ligand and X a univalent anion. The type of complex that forms is dependent on the coordinating ability of the anion. If chloride is utilized, the former prevails, whereas if perchlorate is employed, the latter forms. The two-to-one structure is supported by conductivity data and magnetic susceptibility values (Table I). In contrast, although elemental analyses agree with the formulation of a three-to-one complex, molar conductivity and magnetic susceptibility measurements indicate that they are probably not simple monomeric structures.

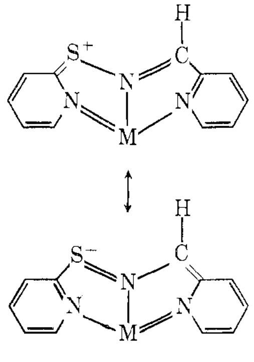
The reaction of 2-sulfenamidopyridine with 2-pyridinaldehyde results in N(2-thiopyridine)2-pyridinalimine. This latter compound functions as a tridentate chelating agent with iron(II), cobalt(II), and nickel(II). If this ligand is viewed as another case of an α-diimine-containing ligand (Va), it is not unexpected that the nickel(II) and cobalt(II) complexes are spin-free octahedral structures, whereas the octahedral iron(II) species is diamagnetic. In consequence, a comparison of this ligand with 2,6-pyridinedialdihydrazone should be valid since the latter is a member of the α-diimine class and contains an additional site of coordination (Vb). Molecular models indicate that the steric requirements of the two molecules nearly approximate each other. Consequently, since both ligands can assume a planar configuration and both coordinate through three imine nitrogen atoms, it is a logical expectation that the properties of the complexes should be nearly alike. A review of the comparable data of the complexes of 2,6-pyridinedialdihydrazone[3] shows this to be the case. Of particular significance is the fact that the values for the splitting parameter of the two nickel complexes are quite similar (1235 cm.$^{-1}$ for the thio derivative as compared to 1250 cm.$^{-1}$ for the dihydrazone). This similarity is quite reasonable if one considers that the relatively high stability of compounds of the α-diimine class is explained as resulting from resonance forms that give rise to partial double bond character in the metal–nitrogen bond, and such canonical forms can be written for both ligands (VI and VII). The same analogy in structure and properties is found to hold true between 2,6-diacetylpyridinedihydrazone and N(2-thiopyridine)2-acetylpyridineimine.[7] In all cases the cobalt and nickel complexes are typical high-spin species, whereas the iron(II) derivatives are diamagnetic.



V

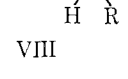


VI



VII

The validity of this comparison resides in the supposition that the electron pair associated with the sulfur atom enters into extensive conjugative interaction with the rest of the molecule. However, an alternative point of view might also be advocated, namely, that the electron pair is localized on the sulfur atom. In this situation, the value for the splitting parameter of the complexes results from an average ligand field derived from a pyridine nucleus which is unconjugated with the α-diimine-containing portion of the molecule. However, the *Dq* value would still be expected to be large due to the presence of this aforementioned α-diimine array. In order to resolve which of these two alternatives is the correct one, a series of aliphatic imines derived from 2-sulfenamidopyridine was synthesized (IV) and their nickel and cobalt complexes of the general formula $(ML_3)(ClO_4)_2$ were prepared. These ligands do not contain the α-diimine grouping but rather the N=C—S—N array. If the electron pair on the sulfur is delocalized to a large extent, then a canonical form can be written (VIII) which equates the N=C—S—N grouping to the α-diimine array. It is then to be expected that the value for the splitting parameter of the nickel complexes of these aliphatic



VIII

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[7] Unpublished data.

imines should approximate analogous complexes with ligands containing the α-diimine arrangement. In contrast, if the electron pair is localized on the sulfur atom, thus precluding conjugation, the *Dq* values for these complexes should be significantly lower. A study of the electronic spectra of the nickel complexes (Table II) shows that there is a large decrease in the value for the splitting parameter when an ethylidene, or other such groups (ES, PS, and BS complex), is substituted for the pyridinal array (TPPI complex). This difference demonstrates that the electron pair is localized on the sulfur atom and does not enter into appreciable conjugation with the rest of the molecule.

The final group of complexes to be discussed results from the reaction of metal perchlorates with N(2-thiopyridine 1-oxide)2-pyridinalimine. This ligand coordinates in a tridentate manner. In addition to the two imine nitrogens coordination also takes place through the N-oxide group. This is supported by infrared spectra, which indicate that the N-oxide stretching frequency is shifted to longer wave lengths for the complexes as compared to the free ligand (Table III), a behavior consistent with that reported for similar N-oxide complexes.[8,9] This behavior is explained as arising from a decrease in the double-bond character of the N–O bond upon coordination.[10]

One additional point is noteworthy. The iron(II) complex is high-spin, a behavior that is rather unusual with ligands containing the α-diimine array. The alteration in the spin multiplicity of this species as compared to the other α-diimine-containing complexes reported herein resides in the nature of the third coordinating atom. In contrast to N(2-thiopyridine)-2-pyridinalimine where chelation occurs through three imine atoms, coordination in N(2-thiopyridine 1-oxide)2-pyridinalimine is through one oxygen and two nitrogen atoms. Therefore, the alteration in properties evolves itself to a difference in the metal–ligand interaction of a pyridine nitrogen atom as contrasted to a N-oxide atom. This alteration is dramatized by the large decrease in the value for the splitting parameter of the nickel complexes of the two ligands. Placing an oxide atom on the pyridine nitrogen results in a decrease in the *Dq* value from 1235 to 980 cm.$^{-1}$. This is consistant with the decrease in the *Dq* value for the hexapyridinenickel(II) ion as compared to the (hexapyridine N-oxide)nickel(II) ion (1015 cm.$^{-1}$ *vs.* 840 cm.$^{-1}$)[11] as well as the tris(bipyridyl)nickel(II) ion as contrasted to the tris(bipyridyl di-N-oxide)nickel(II) ion, where the *Dq* value drops from 1150 to 857 cm.$^{-1}$.[11]

Acknowledgment.—We wish to acknowledge the microanalytical group at Olin Mathieson, who expertly handled and analyzed the explosive samples reported herein.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO 44106

Preparations and Properties of Chromium(II) Complexes. III. Complexes with Dimethyl Sulfoxide[1]

BY DAVID G. HOLAH AND JOHN P. FACKLER, JR.

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Dimethyl sulfoxide (DMSO) complexes of chromium(II) halides have been prepared. These complexes have the stoichiometries $CrCl_2 \cdot 2DMSO$, $CrBr_2 \cdot 3DMSO$, and $CrI_2 \cdot 4DMSO$, but all appear from their visible reflectance spectra to contain six-coordinate, *i.e.*, distorted octahedral, chromium(II). In view of the similarity of chromium(II) and copper(II) chemistry, the DMSO complexes of copper(II) halides have been re-examined and have been found not to contain CuX_4^{2-} as was previously suggested. The complexes $CuCl_2 \cdot 2DMSO$, $CuBr_2 \cdot 2DMSO$, and $CrCl_2 \cdot 2DMSO$ appear to be isomorphous and have similar infrared spectra. The chromium(II) complexes display normal high-spin room temperature magnetic susceptibilities.

Introduction

Since 1960 a large number of dimethyl sulfoxide (DMSO) complexes of first row transition metal salts have been prepared and characterized.[2–8] The ligating properties of DMSO have been discussed and the position of the ligand in the spectrochemical[7] and nephelauxetic[9] series has been established. To our knowledge none of these studies has included work on

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