We resolve the anation reaction (eq 2) into two steps

$$cis\text{-Co(en)}_2\text{NO}_2\text{dmso}^{2+} + \text{X}^- \overset{K}{\rightleftharpoons} cis\text{-Co(en)}_2\text{NO}_2\text{dmso}^{2+},\text{X}^- \qquad (3)$$

$$cis\text{-Co(en)}_2\text{NO}_2\text{dmso}^{2+},\text{X}^- \xrightarrow{k} cis\text{-Co(en)}_2\text{NO}_2\text{X}^+ + \text{dmso}$$

where K is the equilibrium constant for ion association and k is the first-order rate constant for anation. The observed pseudo-first-order rate constants, k_{obsd}, are related to k and K by

$$k_{\text{obsd}} = \frac{kK[\text{X}^-]}{1 + K[\text{X}^-]} \qquad (4)$$

The brackets in (4) represent molar concentrations. It follows that the limiting rate observed with Cl^- and NO_2^- is k. The slope of the thiocyanate plot is kK. (The difficulty we experience in finding k for SCN^- is parallel to the results of Watts, Tobe, and coworkers.)

Values of k for Cl^-, NO_2^-, and SCN^- are, respectively, 5.0×10^{-4}, 1.2×10^{-4}, and $>5.0 \times 10^{-5}$ (probably $<1.0 \times 10^{-4}$; see ref 17). All these values are well below the solvent-exchange rate and span a range of little more than a factor of 2. If one admits that there would be a difference among the anions in the probability of occupancy of the *reactive* site in the ion pair (from the stereochemistry it seems that it would be adjacent to the leaving dmso), the results are accommodated by the I_d model. A model focusing on nucleophilic attack by the anions would face the difficulty that the equilibrium data imply a stronger cobalt–ligand bond to any of the anions than to dmso.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA, UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY

Four-, Five-, and Six-Coordinated Nickel(II) and Cobalt(II) Complexes of Schiff Bases Derived from Pyridine-2-carboxaldehyde and N,N-Substituted Ethylenediamines

BY G. ZAKRZEWSKI[1] AND L. SACCONI

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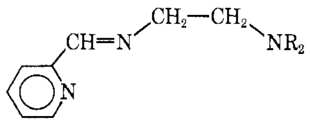
It has been found that tridentate Schiff bases derived from N,N-substituted ethylenediamines and *ortho*-substituted benzaldehydes form pentacoordinate complexes with nickel(II) salts when the terminal nitrogen atom of the ethylenediamine possesses appropriate steric hindrance. Examples of this are the complexes formed with the Schiff bases derived from N,N-diethyl- and N,N-dimethylethylenediamine and *o*-methylaminobenzaldehyde (set NNN),[2] *o*-methylthiobenzaldehyde (set SNN),[3] and *o*-methoxybenzaldehyde (set ONN),[4] respectively. In order to study the stereochemistry of the complexes formed when a heterocyclic nitrogen donor is substituted for a nitrogen donor attached to the ring, we have prepared a new ligand, which is the Schiff base formed from pyridine-2-carboxaldehyde and N,N-dimethyl- and N,N-diethylethylenediamine (I), indicated as PyAenR_2,



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possessing the set of donor atoms NNN. We have also synthesized a similar ligand, derived from furan-2-carboxaldehyde and N,N-dimethylethylenediamine, indicated as FuAenR_2, and possessing the potential set of donor atoms ONN, in order to study its coordinating capacity toward cobalt(II). All of the complexes obtained have the general formula MLX_2 (M = Co, Ni; L = PyAenR_2, FuAenR_2; X = Cl, Br, I, NO_3). During the course of this work two papers regarding pentacoordinate complexes of cobalt(II)[5] and nickel(II)[6] with tridentate ligands containing the pyridyl group have appeared.

Experimental Section

Preparation of the Compounds.—The compounds were prepared by two methods and identical crystalline compounds were always obtained. In the first method equimolar quantities of pyridine-2-carboxaldehyde or furan-2-carboxaldehyde and the appropriate substituted ethylenediamine were heated under reflux for 0.5 hr using ethanol as a solvent. The Schiff base formed in this way was then distilled under vacuum and used without further purification. Samples of 10 mmol of the crude Schiff base and 10 mmol of the appropriate metal halide were dissolved in 50 ml of 1-butanol and heated to boiling. The mixture was concentrated and cooled slowly to obtain needlelike crystals. The complexes were filtered in an atmosphere of dry, pure nitrogen and then dried in a vacuum oven. In the second method of preparation the substituted ethylenediamine, pyridine-2-carboxaldehyde or furan-2-carboxaldehyde, and the metal halide were dissolved in 1-butanol (10 mmol of each compound in 50 ml of solvent); the solution was then heated, concentrated, and cooled. In both cases the yield was about 50–60%.

Physical Measurements.—The electronic spectra, magnetic measurements, and molecular weight and conductometric measurements were performed as reported in ref 2.

Results and Discussion

The analytical data and properties of the complexes are reported in Table I. The complexes are all of the high-spin type. The compounds are soluble in nitroethane and 1,2-dichloroethane and are insoluble in nonpolar solvents. Molecular weight and conductivity values (see Table I) indicate that the complexes are essentially monomeric and nonelectrolytic in solution in inert solvents.

The spectra of the solid compounds are practically identical with those in solution. The halide derivatives show three main peaks at *ca.* 6000, 14,000, and 22,000 cm^{-1} for the nickel complexes (see Figure 1) and

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TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA

Compound	Mol wt	i^a	Mp, °C	Λ^b	% N Calcd	% N Found	% M Calcd	% M Found	μ_{eff}, BM (°C)
$Ni(PyAen(CH_3)_2)Br_2$	394.7	1.08	219–223	0.78	10.64	10.63	14.87	14.66	3.31 (20)
$Ni(PyAen(CH_3)_2)I_2$	488.7	...	242–243	...	8.59	8.44	12.01	11.96	3.28 (20)
$Ni(PyAen(CH_3)_2)(NO_3)_2$	358.9	...	215–220	2.00	19.51	19.20	16.35	15.90	3.22 (18)
$Ni(PyAen(C_2H_5)_2Br_2$	422.8	0.98	202–204	2.01	9.93	9.96	13.88	13.56	3.37 (21)
$Ni(PyAen(C_2H_5)_2I_2$	516.8	...	187–191	...	8.13	8.15	11.35	11.00	3.27 (21)
$Co(PyAen(CH_3)_2)Br_2{}^c$	395.0	0.95	212–214	1.02	10.63	10.64	14.92	14.62	
$Co(PyAen(CH_3)_2)I_2$	488.9	...	222–225	...	8.59	8.62	12.05	11.96	5.05 (20)
$Co(PyAen(C_2H_5)_2)Br_2$	423.0	0.99	194–196	0.48	9.90	9.99	13.93	13.81	4.92 (17)
$Co(PyAen(C_2H_5)_2)I_2$	517.0	...	199–204	...	8.12	8.02	11.39	11.16	4.77 (18)
$Co(FuAen(CH_3)_2)Cl_2$	226.0	...	206–209	0.41	9.46	9.47	19.90	19.75	4.74 (22)
$Co(FuAen(CH_3)_2)Br_2{}^c$	384.9	0.92	226–233	0.13	7.27	7.59	15.30	15.05	4.62 (20)
$Co(FuAen(CH_3)_2)I_2$	478.9	...	220–225	2.79	5.84	6.03	12.30	12.21	4.78 (20)

[a] van't Hoff coefficients for *ca.* 10^{-3} *M* solutions in nitroethane at 37°. [b] All conductivities are reported as cm²/ohm mol. Solutions are *ca.* 10^{-3} *M* and are measured in nitroethane at 25°. The molar conductance of $[(C_4H_9)_4N]Br$ measured using the same temperature and concentration is 68. [c] Values for CH analysis: Calcd for $Co(PyAen(CH_3)_2)Br_2$: C, 30.40; H, 3.57. Found: C, 30.71; H, 3.72. Calcd for $Co(FuAen(CH_3)_2)Br_2$: C, 28.08; H, 3.66. Found: C, 28.03; H, 3.56.

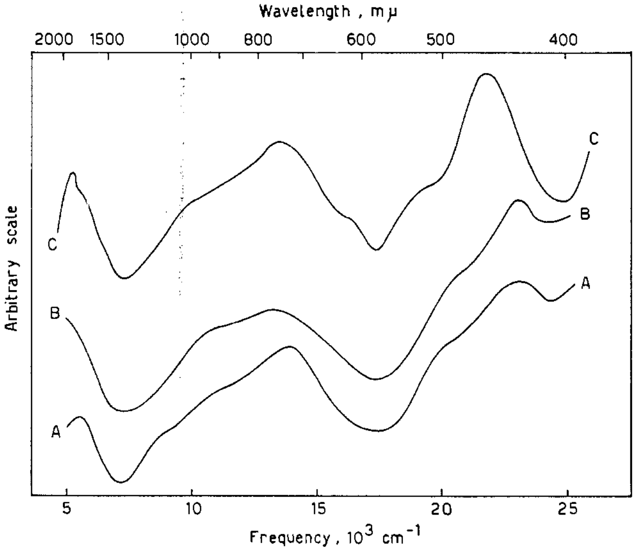

Figure 1.—Reflectance spectra of: $Ni(PyAen(CH_3)_2)Br_2$, curve A; $Ni(PyAen(C_2H_5)_2)Br_2$, curve B; $Ni(Me_5dien)Br_2$, curve C.

maxima at 6000, 8000, 12,000, 16,000, and 21,000 (sh) cm^{-1} for the cobalt ones. The features and absorption frequencies of these spectra are very close to those of the $M(Me_5dien)X_2$ complexes (M = Co, Ni), for which a distorted pentacoordinate structure was ascertained by X-ray structure,[7] and in general to those observed for pentacoordinate complexes of the type MLX_2, where the ligand L has a donor atom set NNN[2-6] and a similar restricting geometry.

Pentacoordinate nickel complexes such as derived from the Schiff bases formed by N,N-diethylethylenediamine and *o*-methoxybenzaldehyde,[4] *o*-methylaminobenzaldehyde,[2] and *o*-methylthiobenzaldehyde,[3] respectively, show in solution and with increasing temperature an equilibrium between pentacoordinate and tetrahedral species. However the spectrum of the nickel complex with $PyAen(CH_3)_2$ remains unchanged as the temperature is raised from 25 to 120°. This can be attributed primarily to the fact that the $PyAen(CH_3)_2$ ligand forms five-membered chelate rings and these are known to be more stable than the six-membered rings which are formed in the above complexes.

The spectrum of $Ni(PyAen(CH_3)_2)(NO_3)_2$ shows bands at 11,000 (ε 24), 16,400 (ε 200), and 25,000 cm^{-1} (ε 110), both in the solid state and in solution. The frequencies and their intensities are characteristic of octahedral complexes.[8] Since the complex, at least in solution, is monomeric and nonconducting, we propose that hexacoordination is achieved by means of a monodentate and a bidentate nitrate group. This is supported by the infrared spectrum which shows four strong bands at 1270, 1320, 1460, and 1515 cm^{-1} attributable to the N–O stretching vibrations. In agreement with the values given by Curtis and Curtis,[9] the two bands at 1270 and 1515 cm^{-1} have been assigned to a bidentate nitrate group and those occurring at 1320 and 1460 cm^{-1} have been assigned to a monodentate group.

The spectra of the $Co(FuAenR_2)X_2$ complexes show bands at *ca.* 6000, 7500, and 10,000 cm^{-1} and a band with more than one maximum at 15,000–17,000 cm^{-1}. These spectra are very similar to those normally found for high-spin pseudo-tetrahedral cobalt complexes of the type CoL_2X_2.[10] On this basis the three bands between 6000 and 10,000 cm^{-1} are assigned to the highest F → F transition (ν_2 in T_d symmetry) and the bands in the region 15,000–17,000 cm^{-1} to the F → P transition (ν_3). The behavior of these furan-2-carboxaldimine ligands toward cobalt(II) is analogous to the *o*-methoxybenzaldimine ligands[4] which have the same potential set of donor atoms ONN. In fact, for cobalt salts with these two ligands, only tetrahedral complexes are obtained when the set is N_2X_2.

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Dimethyl Ether Triborane-7[1]

By W. R. Deever and D. M. Ritter[2]

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This is a report on the preparation and decomposition of dimethyl ether triborane-7. It has proved useful in a number of syntheses where its reactivity was advantageous and the after and side effects of the weakly basic ether were minimal. The preparative result is consistent with earlier observations on similar adducts.[3,4]

Experimental Section

Vacuum line operations were those developed essentially by Stock[5] and by Schlesinger and his co-workers and described by Sanderson[6] and by Jolly.[7]

Melting points were determined at the site of sample formation by visual observation of the temperatures for first appearance of liquid and last appearance of solid.

Tetraborane was prepared by dropping tetramethylammonium triboronate-8 into polyphosphoric acid[8] containing 85% P_2O_5. Dimethyl ether was used directly from a cylinder[9] because it was found free from other substances by glpc analysis.

According to the preferred preparative method tetraborane-10 and dimethyl ether were condensed together at −196°. Then they were warmed to room temperature for 5 min while the vessel was agitated to accomplish thorough mixing. Thereafter the mixture was swiftly cooled to −80°. During the next 2–3 min (depending upon the heat drain) there formed from the liquid a white solid phase, presumably the adduct. Then the temperature was raised to −45°, where it was kept while whatever could be vaporized was removed by high-vacuum pumping during the next 5 hr. The material collected was unreacted tetraborane-10, dimethyl ether, and diborane-6. When instead the reactants were first mixed at −45°, formation of the solid adduct required as long as 2.5 hr. Otherwise the procedure was unchanged. The solid adduct developed negligible vapor pressure (<0.5 mm) until the melting point. The apparent decomposition pressure followed the van't Hoff isochore and reached 29 mm at 24°. Because the processes accompanying vaporization are ill defined, the values[10] have only limited thermochemical use.

Complete decomposition of the adduct (0.24 mmol) occurred within 1 hr at room temperature in a static volume. The products were separated by glpc using mineral oil supported on 80-mesh ground firebrick.

Reaction of boron trifluoride (1.57 mmol) with dimethyl ether triborane-7 (1.25 mmol) was carried out at −16°. Initially there was visible only the solid, but after 30 min there were two liquid phases. Three hours later the products were separated by glpc.

Results

The material balances found in Table I support the belief that the reaction observed was the formation of the 1:1 adduct between dimethyl ether and triborane-7

$$B_4H_{10} + (CH_3)_2O \longrightarrow (H_3C)_2O{-}B_3H_7 + {}^1/_2B_2H_6$$

That an essentially pure solid phase was obtained was attested by the melting range, 10.5–11.1°.

Table I

Stoichiometry of Dimethyl Ether Triborane-7 Formation

B_4H_{10}			$(CH_3)_2O$			B_2H_6
Added[a]	Recovered	Net	Added	Recovered	Net	Recovered
1.51[b]	0.33	1.18	2.13	0.85	1.28	0.59
2.65[c]	0.20	2.45	5.17	2.62	2.45	1.24

[a] All quantities are given in millimoles. [b] Mixed at ≈25°; adduct formed at −80° in 11 ml. [c] Mixed and allowed to react at −45° in 216 ml.

The substances found after decomposition of the adduct and following its reaction with boron trifluoride are to be found in Table II. Other reactions known, but reserved for description elsewhere,[11] are those with diborane and methyldiboranes to give tetraborane and its methyl derivatives and that with trifluorophosphine[12] to give trifluorophosphine diborane-4.

Table II

Products from Reactions of Triborane-7–Dimethyl Ether Adduct

Substance	Decomposition[a,b]	Reaction with BF_3[a,c]
B_2H_6	0.043	0.000
B_4H_{10}	0.055	0.557
B_5H_9	0.016	0.016
B_5H_{11}	0.043	0.134
B_6H_{12}	0.024	0.087
$(CH_3)_2O$	0.234	0.000
Boron recovered as volatile hydrides	0.744	3.510

[a] Quantities in millimoles. [b] From 0.24 mmol of adduct. [c] From 1.25 mmol of adduct, 1.57 mmol of BF_3.

As significant as any substance found is the absence of hydrogen as a product in any of these cases.

In Table III are listed series of reactions suggested to account for the data in Table II. The information presently available does not permit a unique selection from among all reactions possibly contributing to the products. For example, no choice can be made

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[1] Assistance given through NSF Grants GP-3459 and GP-6078 is gratefully acknowledged.

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