Arguments rationalizing weak acceptor character of borate esters in terms of boron–oxygen π bonds are well known and are given elsewhere;[6] however, it is of interest to note that the boron-11 chemical shift data given in Table III for the free heterocycles can be correlated with this rationale, assuming, roughly, that the chemical shift can be considered to be related to the electron density on boron. Chemical shifts for the oxygen-substituted heterocycles occur at significantly higher fields than those for the sulfur-substituted rings $\underline{SCH_2CH_2SB}H$ and $\underline{SCH_2CH_2SB}\text{-}i\text{-}C_4H_9$ suggesting greater electron density around boron in oxygen-substituted heterocycles. This is consistent with the strong acceptor character of $\underline{SCH_2CH_2SB}H$.[7]

TABLE III

BORON-11 NUCLEAR MAGNETIC RESONANCE DATA

Compound	Solvent	J, cps	δ, ppm[a]
$(CH_3O)_2BH$[b]		141	−26.1
$\underline{O(CH_2)_2OB}H$	CH_2Cl_2	173	−28.7
$\underline{O(CH_2)_3OB}H$	CH_2Cl_2	170	−25.9
$\underline{S(CH_2)_2SB}H$	C_6H_6	140	−61.3
$\underline{S(CH_2)_2SB}\text{-}i\text{-}C_4H_9$[c]			−70.0
$\underline{O(CH_2)_2OB}HN(CH_3)_3$	CH_2Cl_2	127	−7.5
$\underline{O(CH_2)_3OB}HN(CH_3)_3$	CH_2Cl_2	152	−16.6

[a] $BF_3 \cdot O(C_2H_5)_2$. [b] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63,** 1533 (1959). [c] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83,** 1345 (1961).

From the dissociation pressure data in Table II, the five-membered ring is apparently a stronger Lewis acid than the six-membered ring, which is consistent with thermochemical studies of the heats of formation of analogous adducts.[2,8]

It is of interest to note that the orders of donor character of tetrahydrofuran, $(CH_2)_4O$, and tetrahydropyran, $(CH_2)_5O$, parallel the order of acceptor character of the boron heterocycles in that the five-membered ring, THF, is a stronger donor than the six-membered ring, THP.[9] Effect of ring size on donor and acceptor character has been accounted for by invoking strain arguments.[2,10,11] However, the only available thermodynamic data suggest that differences in strain energy are very small,[9,12] and other arguments have been invoked to account for the effect of ring size on donor character.[9,13] Essentially, they consider the effect of rehybridization and possible steric factors. The extent to which such arguments are valid has not necessarily been established; however, they can be applied, in principle, to the boron heterocycles as well.

Acknowledgment.—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation.

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Some New Cobalt Nitrosyl Complexes

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During our studies[2-4] of aziridine (ethylenimine) complexes, the possibility of forming some unusual nitrosyl compounds was discovered. A variety of interesting nitrosyl complexes of cobalt have now been prepared. These compounds fit the general formula $CoL_q(NO)_rX_s$, wherein L is a ligand other than nitric oxide and X is one of the anions NO_3^-, Cl^-, or ClO_4^-. The compounds fall into two categories. In one category (hereafter class A), q, r, and s have values of 4, 1, and 2, respectively (if L is bidentate, than $q = 2$). In the other category (hereafter class B), the values of q, r, and s are 2, 2, and 1, respectively.

Experimental Section

Materials.—All materials were obtained commercially. Reagent grade cobalt salts were used without purification. Solid amines were crystallized from appropriate solvents until no further improvement in melting point was obtained. Liquids were distilled prior to use. The amines were distilled over KOH pellets at reduced pressure, and colorless distillates were obtained. Nitric oxide was used as received from Matheson Coleman and Bell.

Procedures.—The compounds were analyzed by Schwarzkopf Microanalytical Laboratory. Infrared spectra were taken in KBr pellets in the range 4000–670 cm^{-1} using a Perkin-Elmer Model 137 spectrophotometer. Magnetic susceptibilities were determined by the Gouy balance technique or pendulum magnetometer at 27–28°. Conductivity measurements were made at 25° in methanol solution on an Industrial Instruments Model RC 16B2 conductivity bridge; the methanol was distilled over Drierite.

Preparations. General.—The reaction vessel consisted of a three-neck flask fitted with a gas inlet tube (extending below the surface of the reaction medium), a dropping funnel, and a gas outlet tube vented to a hood. Reactions were cooled *via* an ice bath, and stirring was accomplished with a Teflon-covered stirring bar and a magnetic stirrer.

Solutions of the appropriate cobalt(II) salt were prepared, filtered, and cooled. The reaction vessel was flushed with N_2. Previously-cooled ligand was added, then the N_2 flow was replaced with NO for the specified period of time. The products were filtered under N_2.

Further details of the preparations may be obtained upon request.[1]

Class A Compounds. Nitrosyltetraaziridinecobalt(II) Chloride Monohydrate, $[Co(C_2H_5N)_4NO]Cl_2 \cdot H_2O$.—To 10 g of

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[1] To whom inquiries should be addressed.

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$CoCl_2 \cdot 6H_2O$ in 100 ml of ethanol was added dropwise 10 g of aziridine in 50 ml of absolute ethanol. NO was passed through for 1.5 hr, then 100 ml of ethyl ether was added, and the mixture was filtered. The product, 12 g of shiny black crystals, was washed with ether and dried *in vacuo* over $CaCl_2$. The compound decomposes vigorously in H_2O and slowly in methanol. It is insoluble in other common organic solvents.

Anal. Calcd for $[Co(C_2H_5N)_4NO]Cl_2 \cdot H_2O$: C, 27.44; H, 6.33; N, 20.00; Cl, 20.25; Co, 16.84. Found: C, 27.63; H, 6.57; N, 19.96; Cl, 20.17; Co, 16.32.

Nitrosyltetraaziridinecobalt(II) Nitrate, $[Co(C_2H_5N)_4NO](NO_3)_2$.—The preparation and properties of this red-brown complex are similar to those of the above chloride.

Anal. Calcd for $[Co(C_2H_5N)_4NO](NO_3)_2$: C, 24.94; H, 5.23; N, 25.45; Co, 15.30. Found: C, 25.05; H, 5.19; N, 25.41; Co, 15.19.

Nitrosylbis(ethylenediamine)cobalt(II) Nitrate, $[Co(C_2H_8N_2)_2NO](NO_3)_2$.—To 10 g of $Co(NO_3)_2 \cdot 6H_2O$ in 120 ml of absolute ethanol was added dropwise 4.1 g of ethylenediamine in 50 ml of absolute ethanol. An NO stream was passed through for 5 hr. Filtering gave 9.5 g of brown-red, crystalline product, which was washed with absolute ethanol and dried *in vacuo* over $CaCl_2$. The solid dissolves in water and methylformamide, less readily in methanol, and very slightly in absolute ethanol, possibly with decomposition in all four. In other common solvents, the material is insoluble.

Anal. Calcd for $[Co(C_2H_8N_2)_2NO](NO_3)_2$: C, 14.42; H, 4.84; N, 29.43; Co, 17.69. Found: C, 14.62; H, 5.16; N, 29.20; Co, 17.44.

Nitrosylbis(ethylenediamine)cobalt(II) Perchlorate, $[Co(C_2H_8N_2)_2NO](ClO_4)_2$.—This compound is a reddish violet solid; the preparation and properties are the same as for the nitrate.

Anal. Calcd for $[Co(C_2H_8N_2)_2NO](ClO_4)_2$: C, 11.77; H, 3.95; N, 17.16; Cl, 17.38; Co, 14.44. Found: C, 11.95; H, 4.12; N, 17.20; Cl, 17.21; Co, 14.19.

Nitrosyltetrapyridinecobalt(II) Perchlorate, $[Co(C_5H_5N)_4NO](ClO_4)_2$.—To 10 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 115 ml of absolute ethanol and 80 ml of ethyl ether was added 8.6 g of pyridine in 40 ml of ethanol. NO was bubbled through for 6 hr. The 4.4 g of pink solid obtained by filtration was washed with ether, then dried *in vacuo* over KOH. The compound reacts readily with moisture in the air, decomposing and releasing NO and pyridine. Decomposition occurs readily in water and organic solvents.

Anal. Calcd for $[Co(C_5H_5N)_4NO](ClO_4)_2$: C, 39.75; H, 3.34; N, 11.59; Cl, 11.73. Found: C, 39.93; H, 3.24; N, 10.97; Cl, 11.34.

Nitrosylbis(*o*-phenylenediamine)cobalt(II) Perchlorate, $[Co(C_6H_8N_2)_2NO](ClO_4)_2$.—*o*-Phenylenediamine (6.5 g) in 100 ml of absolute ethanol was added to 10 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 150 ml of ethanol. NO was passed through for 6 hr. The dark brown-red solid product, which is difficult to obtain pure, was washed with ether and dried *in vacuo* over KOH. The compound decomposes in H_2O and dissolves readily in acetone and methanol, less readily in ethanol. It is insoluble in other organic solvents.

Anal. Calcd for $[Co(C_6H_8N_2)_2NO](ClO_4)_2$: C, 28.59; H, 3.20; N, 13.89; Cl, 14.07; Co, 11.69. Found: C, 28.66; H, 3,47; N, 13.75; Cl, 14.56; Co, 11.45.

Class B Compounds. Dinitrosylbis(*p*-toluidine)cobalt(I) Perchlorate, $[Co(C_7H_9N)_2(NO)_2]ClO_4$.—To 20 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 125 ml of absolute ethanol was added 23.4 g of *p*-toluidine in 75 ml of ethanol, along with 80 ml of ether. NO was passed through for 6 hr, then the mixture was filtered. The 11.2 g of black, shiny needles obtained was washed with ether and dried *in vacuo* over NaOH. The material dissolves in chloroform, ethanol, methanol, acetone, and dichloromethane; no evidence of decomposition was observed. It is insoluble in petroleum ether and carbon tetrachloride. On prolonged exposure to H_2O, it decomposes.

Anal. Calcd for $[Co(C_7H_9N)_2(NO)_2]ClO_4$: C, 38.86; H, 4.19; N, 12.95; Cl, 8.19; Co, 13.62. Found: C, 38.99; H, 3.89; N, 13.38; Cl, 8.11; Co, 13.45.

Dinitrosylbis(aniline)cobalt(I) Perchlorate, $[Co(C_6H_7N)_2(NO)_2]ClO_4$.—These shiny black crystals had the same preparation and properties as the above toluidine complex.

Anal. Calcd for $[Co(C_6H_7N)_2(NO)_2]ClO_4$: C, 35.62; H, 3.49; N, 13.85; Cl, 8.77; Co, 14.56. Found: C, 35.83; H, 3.79; N, 13.90; Cl, 8.56; Co, 14.63.

Dinitrosylbis(triphenylphosphine)cobalt(I) Perchlorate, $[Co[(C_6H_5)_3P]_2(NO)_2]ClO_4$.—Although the compound can be prepared directly, better results were obtained using a ligand replacement method. The *p*-toluidine complex (3 g) was dissolved in CH_2Cl_2 and the solution was filtered. The usual cooling and flushing procedure was followed, then a solution of 5 g of triphenylphosphine in CH_2Cl_2 was added. NO was bubbled through for 5 hr. Upon filtering, 2.9 g of shiny black crystals was obtained, which was washed with ether and dried *in vacuo* over KOH. The compound is soluble in polar organic solvents but not in water or nonpolar solvents.

Anal. Calcd for $[Co(C_{18}H_{15}P)_2(NO)_2]ClO_4$: C, 58.20; H, 4.07; N, 3.77; P, 8.34; Cl, 4.77; Co, 8.34. Found: C, 58.21; H, 4.23; N, 3.93; P, 8.50; Cl, 4.80; Co, 7.74.

Results

Syntheses.—Nine compounds were obtained reproducibly. Some of them tend to decompose in solution, thus purification by recrystallization is not always satisfactory. Nevertheless, some of the compounds form beautiful single crystals and give excellent analyses.

Tributylphosphine gave a complex of the class B type; the complex was, however, an oily liquid. A solid α-naphthylamine complex of class B was prepared; as the analysis indicated some free amine is retained as an impurity, the data will not be given herein. Attempted preparations with hydrazine, *p*-anisidine, methylamine, triethylenetetramine, and a variety of sulfur ligands were not successful.

Properties.—Magnetic data (Table I) indicate that all the compounds are diamagnetic (or very slightly paramagnetic due in all probability to a small amount of spin-free Co(II) impurity). It seems reasonable to conclude that the compounds have diamagnetic ground states.

A single NO stretching frequency[5] was observed with the class A compounds; it is to be noted that the frequency is relatively low (*i.e.*, 1630–1700 cm^{-1}) as compared to the usual[5] range (1700–1900 cm^{-1}). A doublet was found with the class B compounds (see Table I). The NO bands are intense and sharp; in the case of the doublet, the band at lower frequency is more intense. Compounds containing ethylenimine showed the ring vibration in the region of 880–890 cm^{-1}. For the perchlorates of class B, a strong single band of medium width was observed at 1090–1110 cm^{-1}; for the class A perchlorates, the band was in the same region but was more broad. In no case, however, was this vibration split, so we conclude that perchlorate ion is not in the coordination shell.[6] The nitrate vibrations were in those areas which are characteristic of nonbonded nitrate.[7]

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TABLE I

MAGNETIC RESULTS AND INFRARED DATA ON THE COMPLEXES

Compd	Formula	χ, cgs/g × 10^6	NO stretch, cm^{-1}	Relative conductivity
A-1	$[Co(C_2H_5N)_4NO]Cl_2 \cdot H_2O$	−0.18	1630	. . .
A-2	$[Co(C_2H_5N)_4NO](NO_3)_2$	−0.32	1645	. . .
A-3	$[Co(C_2H_8N_2)_2NO](NO_3)_2$	+0.04	1645	. . .
A-4	$[Co(C_2H_8N_2)_2NO](ClO_4)_2$	. . .	1660	194[a]
A-5	$[Co(C_5H_5N)_4NO](ClO_4)_2$	. . .	1700	. . .
A-6	$[Co(C_6H_8N_2)_2NO](ClO_4)_2$	+0.05	1690	160[a]
B-1	$[Co(C_7H_9N)_2(NO)_2]ClO_4$	+0.16	1770, 1850	114[b]
B-2	$[Co(C_6H_7N)_2(NO)_2]ClO_4$	−0.13	1770, 1850	114[b]
B-3	$[Co(C_{18}H_{15}P)_2(NO)_2]ClO_4$	−0.16	1800, 1850	100[b]

[a] Compared to $CaCl_2$ (as 162) at same concentration. [b] Compared to $NaClO_4$ (as 102) and NaI (as 80) at same concentration.

Compounds A-4 and A-6 had conductivities in the range expected for a 2:1 electrolyte; other A class compounds gave erratic conductivity results—possibly due to decomposition. Compounds of class B had conductivities in the range expected for a 1:1 electrolyte.

The compounds are deeply colored, ranging from red-brown to black. It was difficult to obtain satisfactory electronic spectra.

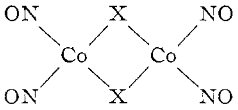
Discussion

The infrared spectra and conductivities suggest that the nitrate and perchlorate anions are not in the coordination sphere. Therefore we have given the name and coordination sphere assignments to be found in the Experimental Section and in Table I.

The compounds reported (with one exception) are new, but they are not without precedent. Booth and Chatt[8] prepared compounds $CoX_2(NO)[P(C_2H_5)_3]_2$, where X = Cl, Br, or I. These may be analogous to our class A complexes; however, the ligands are different and the anions are in the coordination sphere.

After completion of our study, the paper by Feltham and Nyholm[9] was published. In only one case (A-4) was a compound of similar stoichiometry made by both groups. Their data have been interpreted in terms of a polymer with six-coordination about the cobalt atom.

Our class B complexes may be related to the dimeric



(black, diamagnetic crystals) of formula $CoXL(NO)_2$, molecules with X = Cl, Br, or I and to the monomers where L can be phosphines, arsines, stibines, or secondary amines, prepared by Hieber and co-workers.[10,11]

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Aluminum-27 Nuclear Magnetic Resonance Studies of Sodium Fluoride–Aluminum Alkyl Complexes

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Aluminum compounds of the general formula $AlR_{3-N}X_N$ (N = 2–0) will react with certain alkali metal salts to form complex compounds of the types $MX \cdot AlR_3$ and $MX \cdot Al_2R_6$ where M is the metal, X can be hydrogen, halogen, etc., and R is an alkyl such as C_2H_5.[1] The ability to form such complexes depends on several factors such as the size of the alkali and halide ions and the nature of the organoaluminum compound. For example, the tendency of the alkali halides to add to aluminum alkyls increases with the size of the alkali ions and decreases with that of the halogen ions. The stabilities of these complex compounds also decrease as the size of the alkyl group bonded to the aluminum increases.[1]

These complexes are of industrial importance. For example, they can be used for the separation of aluminum alkyls from materials such as olefins and hydrocarbons,[2–5] they can be used as electrolytes for the electroplating of metal objects with aluminum,[6] and they can be used as a source of highly reactive alkyl radicals which can in turn be used in the synthesis of compounds such as tetraethyllead.[7]

This note reports the results of Al^{27} nuclear magnetic resonance (nmr) line-width measurements of several sodium fluoride–aluminum alkyl complexes.

Experimental Section

The Al^{27} nmr measurements were made on a Varian V-4200-A wide-line nmr spectrometer, a Varian 31-cm electromagnet, and a V-2100 power supply. A Varian V-FR2100 Fieldial was used to regulate and scan the magnetic field. A BC-221-D Bendix Radio Corp. frequency meter and Fieldial were used to calibrate and measure the line widths. Temperature at the sample was monitored by passing controlled current through an electric heater in a gas stream directed to the sample in the probe. A resistance-type temperature sensor, near the sample, monitored the gas stream temperature. The temperature control loop was closed around the controller, heater, gas stream, and sensor. The temperatures at the actual sample position were precalibrated with thermocouple and potentiometer. Line widths were measured at 10.0 Mcps and at a magnetic field strength near 9000 gauss. The first derivative of the resonance absorption was recorded using audio modulation (40 cps) of the magnetic field, and the peak-to-peak modulation amplitudes used were between 0.1 and 0.5 gauss. The absorption mode resonances were

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