

ion by chromium(II),²⁷ but additional considerations are in order.

Based on the assumption that the formation of the radical ion intermediate is the rate-determining step and a function solely of ligand and reductant, a proposed criterion to recognize the operation of the radical ion mechanism calls for a comparison of the rate constants for the amine-cobalt(III) complex and the corresponding aquochromium(III) complex.²⁸ A small ratio of cobalt(III) to chromium(III) rates is considered indicative of the importance of the transfer of the electron to the ligand (radical ion mechanism), whereas a large ratio is taken to indicate electron transfer to the metal ion center (resonance exchange mechanism). The reported rate constant for the chromium(II) reduction of $\text{Cr}(\text{OH})_2\text{C}_2\text{O}_4^+$ is $0.13 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° ,²⁹ and therefore the ratio $k_{\text{Co}}/k_{\text{Cr}}$ is $\sim 2 \times 10^6$. On the basis of the proposed criterion, this very high ratio

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would place the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{Cr}^{2+}$ reaction in the resonance-exchange mechanism category. However, it must be noted that the applicability of the proposed criterion to the detection of the radical ion mechanism has been tested in only one case.²⁸ Moreover, the criterion may not be applicable to oxalate ion as a bridging ligand. Since oxalate ion is easily oxidized,³⁰ some contribution of a structure where the oxalate group has relinquished an electron to the oxidizing center would be considerably more important for $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ than for $\text{Cr}(\text{OH})_2\text{C}_2\text{O}_4^+$, and this factor may account for the large $k_{\text{Co}}/k_{\text{Cr}}$ ratio. If this argument is accepted, the suggestion that the chromium(II) reductions proceed by the radical ion mechanism must still be considered as tentative.³¹ As repeatedly emphasized, conclusions based solely on reactivity patterns and rate comparisons may be unreliable.

(30) For the spontaneous oxidation of oxalate bound to cobalt(III), see J. Aggett and A. L. Odell, *J. Chem. Soc., A*, 1415 (1968).

(31) Our suggestion of a radical ion mechanism would appear, at first glance, to contradict the conclusions reached previously⁸ regarding the reactions of Cr^{2+} with $\text{Co}(\text{NH}_3)_4\text{CO}_2\text{COX}^{2+}$ ($\text{X} = \text{O}, \text{OH}, \text{CH}_3, \text{NH}_2, \text{C}(\text{CH}_3)_3$). However, it must be noted that Price and Taube⁸ concluded that not all of their observations could be accommodated by the radical ion mechanism.

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Cobalt(II) Complexes of the Quadridentate Macrocyclic 2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene¹

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Received September 9, 1969

A series of cobalt(II) complexes of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene, CR, have been prepared; all are low spin in electronic configuration. The electronic spectra have been interpreted with the aid of an energy level diagram for trigonal-bipyramidal, low-spin cobalt(II), d^7 . Pentacoordination is supported by conductance measurements in several solvents. The low magnetic susceptibilities of the solids $\text{Co}(\text{CR})\text{BrX}$ ($\text{X}^- = \text{ClO}_4^-, \text{PF}_6^-, \text{B}(\text{C}_6\text{H}_5)_4^-$) indicate a cobalt-cobalt interaction in these compounds.

Introduction

Although nickel(II) derivatives of the newer synthetic macrocycles dominated initial studies,³ recently a number of cobalt complexes have been reported.⁴⁻¹³ Most of these have been cobalt(III) derivatives with *meso*- and *dl*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-

azacyclotetradecane (7,14-CTH),^{4,5} with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene (1,7-CT),⁶ with 1,4,8,11-tetraazacyclotetradecane (cyclam),⁷ with 1,4,7,10-tetraazacyclododecane (cyclen),⁸ and with *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (CRH).⁹ However, some cobalt(II) derivatives have been reported with the macrocycles 1,7-CT,¹⁰ *meso*-7,14-CTH,¹¹ and 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-diene (1,4-CT).¹² The *meso*-7,14-CTH complexes are generally low spin with normal Curie-Weiss behavior.¹¹

The present work was undertaken as part of a general program concerned with investigation of the characteristics of macrocyclic cobalt(II) complexes. The ligand studied, 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR, structure I), was first known in its copper(II)¹³ and

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(2) National Institutes of Health Predoctoral Fellow, 1965-1967.

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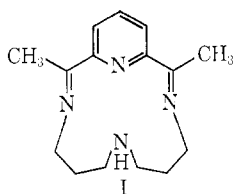
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nickel(II) complexes.^{14,15}

Results and Discussion

Complexes of the tetradentate, macrocyclic ligand 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR) with cobalt(II) and zinc(II) were prepared and their magnetic, spectral, and solution properties have been investigated. Three series of cobalt(II) complexes have been characterized: $\text{Co}(\text{CR})\text{X}_2 \cdot n\text{H}_2\text{O}$ with $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{NCS}^-, \text{or } \text{ClO}_4^-$ and $n = 0, 0.5, \text{ or } 1$; $\text{Co}(\text{CR})\text{A}(\text{ClO}_4)_2$ with $\text{A} = \text{NH}_3$ or pyridine (py); and $\text{Co}(\text{CR})\text{BrX}$ with $\text{X}^- = \text{ClO}_4^-, \text{PF}_6^-, \text{ or } \text{B}(\text{C}_6\text{H}_5)_4^-$. All of these complexes contain low-spin cobalt(II), d^7 , and are pentacoordinate. The azo-methine linkages of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ and of $\text{Co}(\text{CR})\text{I}_2$ have been hydrogenated. One zinc complex, $\text{Zn}(\text{CR})\text{I}_2$, has been prepared and characterized.

Syntheses.—In the $\text{Co}(\text{CR})\text{X}_2 \cdot n\text{H}_2\text{O}$ series of compounds, four of the products were prepared by synthesizing the macrocyclic ligand in the presence of an appropriate cobalt(II) salt. $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ and $\text{Co}(\text{CR})(\text{NCS})_2$ were prepared with CoBr_2 and $\text{Co}(\text{NCS})_2$, respectively, while $\text{Co}(\text{CR})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ and $\text{Co}(\text{CR})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ were prepared from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In each case, the cobalt(II) salt, 2,6-diacetylpyridine, and 3,3'-diaminodipropylamine in a 1:1:1 mole ratio were heated at 65–75° in aqueous ethanol, following Karn's procedure for synthesis of $\text{Ni}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$.¹⁴ Some water was necessary to prevent precipitation of the intermediate complex of diacetylpyridine and cobalt(II). All steps involving solutions of cobalt(II) were carried out in a purified nitrogen atmosphere unless otherwise stated. A little acetic acid was added to the reaction mixture to buffer the amine solution and to catalyze the Schiff base condensation. After a 4–6-hr heating period, the solution was concentrated under reduced pressure to about half of its initial volume. Upon cooling the concentrated solution, the black thiocyanato and nitrate complexes crystallized. The black bromo complex was obtained by adding a concentrated ethanolic solution of lithium bromide to induce crystallization of the product. To obtain the perchlorate, the volume of the reaction mixture was reduced until the solution was very concentrated, so that nearly all of the ethanol was removed. This minimized the possibility of the formation of perchlorate esters due to the presence of acetic acid and the sodium perchlorate that was to be added, but the solution should be handled cautiously. To the hot solution, a concentrated aqueous solution of sodium

perchlorate was added and the maroon product crystallized very rapidly.

The remaining complexes were prepared by metathetical reactions. The bromo complex $\text{Co}(\text{CT})\text{Br}_2 \cdot \text{H}_2\text{O}$ was the starting material for the iodo and ammine complexes and the $\text{Co}(\text{CR})\text{BrX}$ complexes. The other derivatives were prepared from the aquo complex, $\text{Co}(\text{CR})\text{OH}_2(\text{ClO}_4)_2$. It is interesting that large excesses of ammonia and pyridine did not cause formation of bis adducts.

Infrared Spectra.—The infrared spectra of the cobalt(II) complexes are quite similar to each other with the exception of bands which may be assigned to monodentate ligands or to anions. The spectra are also somewhat like that of $\text{Ni}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$, as reported by Karn.¹⁴ Resolved OH stretching bands are characteristic of this compound and of the corresponding chloro and nitrate derivatives, while $\text{Co}(\text{CR})\text{OH}_2(\text{ClO}_4)_2$ has an unresolved, broadened OH stretching band. The remaining compounds are anhydrous.

The NH stretching frequencies range from 3145 and 3150 cm^{-1} in the thiocyanato and nitrate complexes to 3230 and 3224 cm^{-1} in the aquo and pyridine complexes, with an average value of 3187 cm^{-1} . The low values are with anions which can readily form hydrogen bonds with the secondary amine proton. On the other hand, the high values are with neutral ligands which cannot readily form hydrogen bonds once they are coordinated to the cobalt(II) ion. The remaining complexes have NH stretching frequencies very near the average, 3175–3195 cm^{-1} .

Bands at 1570–1580, ~1470, ~1425, and ~1205 cm^{-1} are assigned to pyridine ring vibrations.¹⁶ The band between 1570 and 1580 cm^{-1} is obviously complex and coincides with the stretching vibration of the azo-methine groups, as evidenced by the decrease in its intensity upon hydrogenation of the azo-methine linkages. This is an unusually low frequency for a C=N moiety since it is usually found near 1660 cm^{-1} .¹⁶

In the aquo complex (perchlorate salt), a strong band is present at 1047 cm^{-1} , near a very strong broad band at 1100 cm^{-1} . The latter is assigned to ionic perchlorate and one might assume that the former is due to a coordinated perchlorate. However, the fact that a strong band is often observed near 1050 cm^{-1} in these cobalt(II) complexes, the fact that the band near 940 cm^{-1} is not enhanced compared to other spectra, and the absence of substantial splitting of the ν_1 band of the perchlorate ion at 623 cm^{-1} indicate that the perchlorate ions are equivalent and uncoordinated.^{17–19}

Magnetic Properties.—Low-spin electronic configurations are indicated by the effective magnetic moments at room temperature, Table I. All of the solid-state moments have standard deviations of ± 0.05 BM or

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TABLE I
 MAGNETIC MOMENTS OF Co(CR)²⁺ DERIVATIVES

Compound	μ_{eff} , BM	Compound	μ_{eff} , BM
Co(CR)Cl ₂ ·H ₂ O	2.09 ± 0.00 ^{a,c}	Co(CR)NH ₃ (ClO ₄) ₂	1.93 ± 0.02 ^a
Co(CR)Br(ClO ₄)	2.06 ± 0.07 ^b	Co(CR)py(ClO ₄) ₂	1.91 ± 0.01 ^a
Co(CR)Br ₂ ·H ₂ O	2.05 ± 0.05 ^b	Co(CR)(NCS) ₂	1.76 ± 0.01 ^a
Co(CR)OH ₂ (ClO ₄) ₂	2.03 ± 0.05 ^a	Co(CR)Br(B(C ₆ H ₅) ₄)	1.20 ± 0.15 ^a
Co(CR)(NO ₃) ₂ ·0.5H ₂ O	2.02 ± 0.01 ^a	Co(CR)Br(ClO ₄)	1.07 ± 0.02 ^a
Co(CR)I ₂	2.01 ± 0.03 ^a	Co(CR)Br(PF ₆)	1.05 ± 0.02 ^a
Co(CR)Br ₂ ·H ₂ O	2.00 ± 0.03 ^a		

^a Solid state. ^b Aqueous solution. ^c Faraday method; all others by Gouy method.

less, except for the tetraphenylborate salt. Owing to the small amount of the chloro complex available and its hygroscopic nature, its susceptibility was determined by the Faraday method. All of the other susceptibilities have been determined by the Gouy method, using mercury(II) tetrathiocyanatocobaltate(II) as standard. Each complex compound has been packed in the glove box, using a dry sample which had never been exposed to air. The calculated magnetic moments are the same, within experimental error, as those obtained with samples packed in air.

Little variation is noted among the effective magnetic moments of most of the complexes. The highest value, 2.09 BM is exhibited by the chloro complex. Clustered very close together are values for Co(CR)OH₂(ClO₄)₂, Co(CR)(NO₃)₂·0.5H₂O, Co(CR)I₂, and Co(CR)Br₂·H₂O, all at about 2.0 BM. Slightly below this value are those for Co(CR)NH₃(ClO₄)₂ and Co(CR)py(ClO₄)₂ whose moments approximate 1.9 BM. These values all exceed that of Co(CR)(NCS)₂, 1.76 BM, which is very close to the spin-only value for one electron. These moments are consistent with the values reported for low-spin penta- and hexacoordinated cobalt(II) but are lower than those generally reported for presumed square-planar cobalt(II).²⁰⁻²³

The complexes of the type Co(CR)BrX are strikingly different, with solid-state, room-temperature moments (per cobalt ion) slightly over 1 BM. In aqueous solution (9.46 × 10⁻³ weight fraction of complex), the perchlorate salt, Co(CR)Br(ClO₄), exhibits an effective magnetic moment of 2.06 ± 0.07 BM. The PF₆⁻ and B(C₆H₅)₄⁻ salts are not sufficiently soluble in water to permit determination of their susceptibilities in solution. Measurements on a similar solution with 1.15 × 10⁻² weight fraction of Co(CR)Br₂·H₂O give a moment of 2.05 ± 0.05 BM. Also, it should be noted that the solid-state moment of the aquo complex Co(CR)OH₂(ClO₄)₂ is 2.03 ± 0.05 BM.

The temperature dependence of the magnetic susceptibility of Co(CR)BrClO₄ was determined. A plot of the reciprocal of the corrected molar susceptibility vs. temperature gave a line with a slope of (-1.54 ± 0.19) × 10⁻³ cgsu⁻¹ deg⁻¹ and an intercept of (2.22 ± 0.10) × 10³ cgsu⁻¹. This predicts an effective magnetic moment per cobalt ion of about 0.06 BM at 1°K

and a value corresponding to one unpaired electron at about 500°K.

This evidence indicates that in the solid state there is some interaction between cobalt(II) ions that reduces the magnetic moment to an abnormally low value for certain complexes of this macrocyclic ligand. A change of this nature in the magnetic moment in going from the solid state to solution is known for other cobalt(II) compounds. Potassium pentacyanocobaltate(II) has a reported magnetic susceptibility of -0.196 × 10⁶ cgsu in the solid state.²⁴ This corresponds to an effective magnetic moment of 0.35 BM at room temperature. In dilute aqueous KCN solution, the susceptibility is reported as 1240 × 10⁶ cgsu, corresponding to a magnetic moment of 1.72 BM per cobalt ion, essentially the spin-only value for one electron.²⁴ Alexander and Gray have examined the esr spectrum in ethylene glycol-water and ethylene glycol solutions at 300 and at 77°K. On the basis of *g* values, *g*_{||} = 1.992 ± 0.005 and *g*_⊥ = 2.157 ± 0.005, they assigned a ²A₁ ground state to the complex with square-pyramidal geometry in solution. They rejected a trigonal-bipyramidal geometry as giving rise to a ²E₁' ground state which would be expected to have *g*_{||} >> 2.0.²⁵

Similar diamagnetic and paramagnetic species are observed with pentakis(methyl isocyanide)cobalt(II) perchlorate. A red, dimeric form is known in the solid state. It can be converted to a blue form with an effective magnetic moment of 1.72 BM.²⁶ The structure of the red solid is reported to be "bioctahedral" with one Co(CNCH₃)₅²⁺ unit rotated by 45° with respect to the other. The two units are joined by a cobalt-cobalt bond to form the dimer that is present in the solid state.²⁷

The recently reported magnetic moments of the claimed dimeric cobalt(II) complexes with 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-diene (1,4-CT) range from "approximately zero" to 4.86 BM per dimer. The low values are for the thiocyanato and cyano complexes, X⁻ = NCS⁻ or CN⁻ in [XCo(1,4-CT)]₂²⁺, approximately zero and 0.84 BM, respectively, per dimeric unit. The latter has recently been shown to be the cobalt(III) complex [Co(1,4-CT)(CN)₂]₂ClO₄.²⁸ The claimed dimer of Co(TAAB)-

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TABLE II
 ELECTRONIC SPECTRA OF Co(CR)²⁺ DERIVATIVES

Compound	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}
Co(CR)I ₂ ^a	7,320 (1.00) ^e	11,600 (1.59) ^e	13,250 (1.81) ^e	15,400 (2.10) ^a
Co(CR)Br ₂ ·H ₂ O ^a	8,700 (1.00)	13,800 (1.59)	15,900 (1.83)	17,600 (2.02)
Co(CR)Br ₂ ·H ₂ O ^b	9,010 (1.00)	14,400 (1.60)	16,400 (1.82)	17,800 (1.97)
Co(CR)Br(ClO ₄) ^a	8,700 (1.00)	14,200 (1.63)	16,200 (1.86)	18,000 (2.07)
Co(CR)Br(PF ₆) ^c	9,260 (1.00)	14,000 (1.51)	16,000 (1.73)	17,500 (1.89)
Co(CR)Br(B(C ₆ H ₅) ₄) ^a	8,770 (1.00)	14,000 (1.60)	16,100 (1.84)	17,900 (2.04)
Co(CR)Cl ₂ ·H ₂ O ^a	9,100 (1.00)	13,700 (1.51)	15,650 (1.72)	16,900 (1.86)
Co(CR)Cl ₂ ·H ₂ O ^b	9,570 (1.00)	14,300 (1.50)	16,300 (1.70)	17,700 (1.85)
Co(CR)(NO ₃) ₂ ·0.5H ₂ O ^a	9,260 (1.00)	14,000 (1.51)	16,000 (1.73)	17,900 (1.93)
Co(CR)(NO ₃) ₂ ·0.5H ₂ O ^b	9,900 (1.00)	14,410 (1.45)	16,400 (1.67)	18,300 (1.85)
Co(CR)OH ₂ (ClO ₄) ₂ ^a	8,850 (1.00)	14,500 (1.64)	16,500 (1.86)	18,700 (2.11)
Co(CR)(NCS) ₂ ^a	9,440 (1.00)	14,400 (1.53)	16,200 (1.72)	17,700 (1.88)
Co(CR)(NCS) ₂ ^b	9,620 (1.00)	14,700 (1.53)	16,600 (1.73)	18,000 (1.87)
Co(CR)py(ClO ₄) ₂ ^a	9,710 (1.00)	14,500 (1.49)	16,100 (1.66)	18,000 (1.85)
Co(CR)NH ₃ (ClO ₄) ^c	9,660 (1.00)	14,700 (1.52)	16,880 (1.74)	18,300 (1.90)
Co(CR)NH ₃ (ClO ₄) ^d	10,100 (1.00)	15,500 (1.54)	18,000 (1.78)	21,400 (2.12)

^a Reflectance spectrum. ^b Methanol solution. ^c Nujol mull spectrum. ^d Acetonitrile solution. ^e Ratio of ν_n/ν_1 , $n = 1, 2, 3, 4$.

Br₂ was erroneously formulated.²⁹ It is also a cobalt(III) complex.

Solution magnetic susceptibilities for the 1,4-CT dimers are not reported, but the unreported visible spectra in water, methanol, and acetone are said to be different, implying that the dimers solvate in these solvents.¹²

The data reported here indicate that the cobalt-cobalt interaction in Co(CR)X⁺ is negligible in aqueous solution. In pentacoordinate structures with CR in unstrained configurations and with one unidentate ligand coordinated, stereomodels indicate that any cobalt-cobalt interaction would have to be over a rather long distance. This would limit overlap and might fail to stabilize the singlet state completely. These conclusions are also supported by conductance measurements reported below.

Electronic Spectra.—Solid and solution electronic spectra have been recorded with a Cary 14 recording spectrophotometer. Reflectance spectra cover the wavelength range from 2000 to 330 m μ , and Nujol mull diffuse transmittance spectra cover the range from 1600 to 240 m μ . The range covered by solution spectra varied with range of transparency of the solvent.

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In both the solid state and in solution, the electronic spectra show a weak band in the near-infrared region at about 9000 cm⁻¹, a series of closely spaced bands in the visible region, and some very intense bands in the ultraviolet range, Table II and Figure 1. These spectra are quite unlike that of hexacoordinate, low-spin cobalt(II) in Co(NO₂)₆⁴⁻. This octahedral ion has weak bands assigned to d-d transitions at 7000–8000, 15,000–16,000, and 18,000 cm⁻¹³⁰ and stronger bands at 23,000, 28,400, 34,400, 39,900, and 49,500 cm⁻¹. These more intense bands are assigned to charge-transfer transitions.³¹ Reported spectra for high-spin, pentacoordinate complexes are also quite different; e.g., dichloro-1,1,7,7-tetraethyldiethylenetriamincobalt(II) has bands at 11,200 (18), 15,300 (58), and 19,050 cm⁻¹ (60) in its ethanol solution spectrum.³¹ Square-pyramidal Co(dpe)₂Br₂ (dpe = bis(diphenylphosphino)ethane) has absorption bands at 4760, 6850, 14,700, 15,400, and 22,750 cm⁻¹ in a Nujol mull spectrum.³² On the other hand, the spectra of Co(CR)X⁺ (X⁻ = Cl⁻, Br⁻, I⁻, NO₃⁻, NCS⁻) and Co(CR)A²⁺ (A = NH₃, py, OH₂) are remarkably like the published spectra of low-spin complexes of tris(*o*-diphenylphosphinophenyl)phosphine (QP), CoX(QP)⁺, with X⁻ = Br⁻²¹ or NO₃⁻.³³ CoX(QP)⁺ spectra show a broad band at about 10,000 cm⁻¹ and what are evidently complex bands at about 15,000 and 20,000 cm⁻¹. The extinction coefficients of the absorptions in the near-infrared and visible regions are about five to ten times greater than those reported here, Figure 1. These QP complexes have a trigonal-bipyramidal geometry about the cobalt(II) ion.³⁴ Norgett, Thornley, and Venanzi³³ have constructed an energy level diagram for trigonal-bipyramidal complexes of low-spin cobalt(II), d⁷, using a crystal field model. They did not assign term states for the various energy levels.

This model predicts one low-energy band with less intensity than that of a group of five closely spaced bands at higher energy. One-electron transitions are expected to occur at the frequency ratios of 1.00:1.61:1.82:1.97, where the frequency ratio is defined as ν_n/ν_1 for $n = 1, 2, 3$, and 4. Frequency ratios have been calculated for the absorption bands of all the CR complexes whose solid-state spectra are summarized in Table II. The range varies from 1.49 to 1.64 for the second band, from 1.66 to 1.86 for the third band, and from 1.85 to 2.11 for the fourth observable band. The average ratios are 1.00:1.56:1.77:1.97, which compare quite well with the predicted values. In only five cases—Co(CR)X₂·*n*H₂O with X⁻ = Br⁻, Cl⁻, NCS⁻, and NO₃⁻ and Co(CR)NH₃(ClO₄)₂—are the compounds soluble enough to observe all of the first four bands in solution. In these, the frequency ratios range from 1.45 to 1.60, 1.67 to 1.82, and 1.85 to 2.12 for the second,

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(31) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

(32) W. D. Horrocks, Jr., G. R. Van Horke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967).

(33) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc. A*, 540 (1967).

(34) L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964).

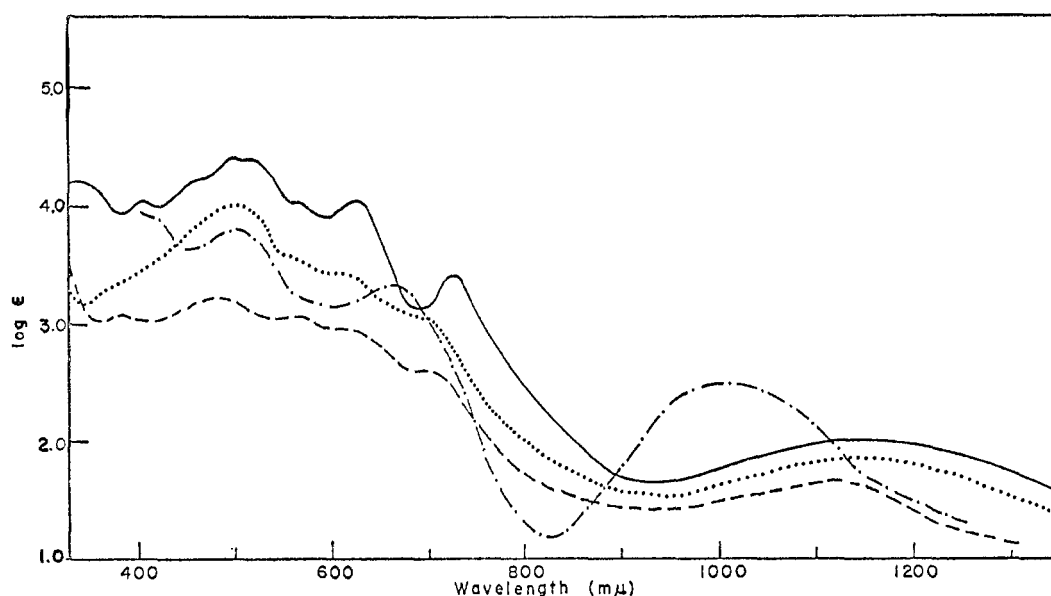


Figure 1.—Electronic spectra: —, $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ (solid); ···, $\text{Co}(\text{CR})\text{Br}(\text{ClO}_4)$ (solid); ---, $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ (in CH_3OH); -·-·, $\text{Co}(\text{NO}_3)\text{QP}^+$ (in CH_2Cl_2 ; from R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964)).

third, and fourth observable bands, respectively. They average 1.00:1.52:1.72:1.93. In those cases where the ratio of the "fourth band" to the first is quite large (~ 2.1), a different transition may be responsible for the absorption, replacing the transition observed where the ratio is smaller. On this basis, ν_1 is assigned to the transition from the $(e'')^4(e')^3$ ground-state configuration to the $(e'')^3(e')^4$ configuration of the first excited state in idealized D_{3h} symmetry. The remaining ligand field bands are assigned to the transitions from the ground state to doublet states arising from the configurations $(e'')^4(e')^2(a'_1)$ and $(d'')^3(e')^3(a'_1)$. From these correlations of the electronic spectra of $\text{Co}(\text{CR})\text{X}^+$ and of $\text{Co}(\text{CR})\text{A}^{2+}$, the cobalt(II) ion must be pentacoordinate with a geometry perhaps best described as that of a distorted trigonal bipyramid.

Both in solution and in the solid state, the electronic spectra of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ and of $\text{Co}(\text{CR})\text{BrX}$ ($\text{X}^- = \text{ClO}_4^-, \text{PF}_6^-, \text{and } \text{B}(\text{C}_6\text{H}_5)_4^-$) are similar, Figure 1 and Table II. However, the absorption bands in the latter group of complexes tend to occur at slightly higher frequencies and to have slightly lower intensities. Thus the ligand fields must be quite similar in all of these bromide-containing complexes and pentacoordination of the nitrogen and bromide donors is expected of all of them. Previously reported pentacoordinate cobalt(II) complexes with three or more nitrogen donors have been high spin, with magnetic moments between 4 and 5 BM.^{31,35} The compounds reported here are unique in containing low-spin, pentacoordinate cobalt(II) with four or five nitrogen donors.

Conductivity Studies.—Pentacoordination of the $\text{Co}(\text{CR})\text{X}_2$ and $\text{Co}(\text{CR})\text{A}(\text{ClO}_4)_2$ compounds is supported by the conductance data summarized in Table III. The $\text{Co}(\text{CR})\text{X}_2$ complexes ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{NCS}^-$) are all uni-univalent electrolytes in nitromethane, DMF, and/or methanol, while the Co -

$(\text{CR})\text{A}(\text{ClO}_4)_2$ complexes ($\text{A} = \text{NH}_3, \text{py}, \text{or } \text{OH}_2$) are all di-univalent electrolytes in nitromethane, DMF, and/or methanol.

TABLE III
MOLAR CONDUCTANCES^a OF THE NEW COBALT(II)
COMPOUNDS, $\text{Co}(\text{CR})\text{XY}_m \cdot n\text{H}_2\text{O}$

X	Y_m	n	Solvent			
			CH_3OH	H_2O	CH_3NO_2	DMF
I^-	I^-	0			82.6	80.2
Br^-	Br^-	1	104	220	97.2	61.4
Br^-	ClO_4^-	0		208	94.2	80.2
Br^-	PF_6^-	0			94.2	
Br^-	$\text{B}(\text{C}_6\text{H}_5)_4^-$	0			70.8	
Cl^-	Cl^-	1	90.5			
NO_3^-	NO_3^-	0.5			72.7	
OH_2	$(\text{ClO}_4^-)_2$	0	178		176	146
NCS^-	NCS^-	0				66.6
py	$(\text{ClO}_4^-)_2$	0			172	
NH_3	$(\text{ClO}_4^-)_2$	0			163	

^a Approximately $10^{-3} M$ solutions, in $\text{cm}^2/\text{ohm mol}$.

If the formulation of $\text{Co}(\text{CR})\text{BrX}$ is assumed on the basis of elemental analyses and the electronic spectra, the conductances imply that these complexes are uni-univalent electrolytes in nitromethane (and in DMF for $\text{X}^- = \text{ClO}_4^-$).

A study of the effect of concentration on the equivalent conductance of the perchlorate salt in nitromethane discloses some dissociation effects at concentrations below $10^{-4} M$ in cobalt(II). Between 9×10^{-4} and $4 \times 10^{-3} M$, a plot of the equivalent conductance (Λ_e) vs. the square root of the concentration is linear, with a least-squares value of 108 ohm^{-1} at infinite dilution (Λ_0). At $10^{-2} M$, the equivalent conductance drifts to somewhat lower values, indicating increased association. Using the method of Feltham and Hayter,³⁶ a plot of $\Lambda_0 - \Lambda_e$ vs. the square root of the concentration gives, by least squares, a line with a

(35) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967).

(36) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

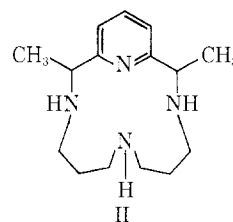
slope of 476. Feltham and Hayter's standard divalent electrolytes in nitromethane had slopes of 420, 465, and 510 in such plots. Thus the proper formulation of the compound reported here is $[\text{Co}(\text{CR})\text{Br}]_2(\text{ClO}_4)_2$ in nitromethane solution at intermediate concentrations. The electronic spectrum of this compound in nitromethane is incomplete due to the lower intensities found in this solvent. Only faint shoulders are discernible, with molar extinction coefficients that are less than one-tenth of those found for the same bands in methanol solution. However, the bands observed in the nitromethane solution are in the same position as two of the bands in the reflectance spectrum implying that no change in coordination has occurred. The magnetic susceptibility was not determined in nitromethane due to the very great sensitivity to air oxidation of cobalt(II) in this solvent and the difficulty in excluding air for the length of time necessary for the determination. In water, $\text{Co}(\text{CR})\text{Br}(\text{ClO}_4)$ and $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ have similar molar conductances of 208 and 220 ohm^{-1} , respectively. This implies aquation of the complex cations, forming $\text{Co}(\text{CR})\text{OH}_2^{2+}$ in each case. The electronic spectra of aqueous solutions of these compounds are identical.

Thus, there must be a cobalt-cobalt interaction in nitromethane solution, probably similar to the interaction in the solid state. The intermediate solid-state magnetic susceptibility must be due to this interaction—a limited overlap of the singly occupied orbitals of the cobalt(II) ions. From the molar conductances and the magnetic susceptibilities in aqueous solution, the dimer must be dissociated in water, giving a negligible interaction between the metal ions in this magnetically dilute environment.

Hydrate Phenomena.—In $\text{Ni}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$, the occurrence of two distinct OH stretching vibrations has been interpreted as being due to the fixed position of the water molecules in the crystal. Contrary to Karn's conclusions,¹⁴ the water can be removed from this complex, as well as from the corresponding cobalt(II) complex, at 100° *in vacuo*. This was demonstrated by means of a Nujol mull spectrum of the dried and carefully protected material, where the OH stretching and deformation bands were absent. The weight loss on drying was $3.5 \pm 0.3\%$ (calculated 3.6%). The OH stretching and deformation bands reappear rapidly upon exposure of the solid, dispersed in Nujol oil, to ambient air. The easy vapor-phase exchange of the water with D_2O confirms that there must be a facile transport mode *within* the solid. Deuterated nickel(II) and cobalt(II) complexes rapidly exchange their D_2O with water vapor in the air. This also happens with $dl\text{-Ni}(1,7\text{-CT})(\text{NCS})_2 \cdot \text{D}_2\text{O}$ and explains the appearance of the "strong unassigned bands" that were reported by Curtis and Curtis in the OH stretching region.³⁷

Hydrogenation of the Azo-Methine Linkages.—Hydrogen smoothly reduces the azo-methine linkages of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ in methanol solution with PtO_2 catalyst. A decrease in the hydrogen pressure in the Parr

hydrogenation apparatus, a decrease in the intensity of the infrared band at 1575 cm^{-1} , and increases in the intensities of the NH stretching and deformation bands indicate that hydrogenation has occurred. These observations are similar to those of Karn when he reduced $\text{Ni}(\text{CR})(\text{ClO}_4)_2$ in aqueous solution with the same catalyst.^{14,15} The resulting halo-2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]-heptadeca-1(17),13,15-trienecobalt(II) ions, $\text{Co}(\text{CRH})\text{X}^+$, can be isolated easily as the hexafluorophosphate salts. The ligand structure is given in II. Isolation of $\text{Co}(\text{CRH})\text{Br}_2$ is



more difficult because of its high solubility in methanol. It is necessary to reduce the volume of the solution greatly to induce formation of the microcrystalline, reddish brown solid. $\text{Co}(\text{CRH})\text{Br}_2$ has a molar conductance of 86.1 ohm^{-1} in methanol which indicates that it is a uni-univalent electrolyte in this solvent. Its effective magnetic moment is 2.05 BM at room temperature. This solid-state moment is slightly higher than that of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$. It should also be noted that the hydrogenated bromide complex is anhydrous.

Two features are noticeable in the electronic spectrum of $\text{Co}(\text{CRH})\text{Br}_2$. The first band in the mull spectrum is about 8300 cm^{-1} (vb), which is about 400 cm^{-1} lower in energy than the first transition observed in $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$, confirming that the ligand field of CR is greater than that of CRH.⁸ Second, the spectrum appears to be simpler, with fewer bands and lower molar extinction coefficients for the band in the visible region. The second band of the solid-state spectrum is not observed in the solution spectrum, perhaps because of its low extinction coefficient, for it is barely visible in the Nujol mull spectrum.

Zinc(II) Complex.—A single zinc complex has been prepared, bright yellow $\text{Zn}(\text{CR})\text{I}_2$. It is a uni-univalent electrolyte in DMF ($\Lambda_0 = 80.4 \text{ ohm}^{-1}$) and is only slightly soluble in other solvents. A water solution is nearly saturated at 10^{-5} M . In aqueous solution, the ultraviolet spectrum has bands at $\sim 32,400$ (~ 3420), $33,600$ (4760), $\sim 34,600$ (~ 4030), and $44,900 \text{ cm}^{-1}$ (40,000). For comparison, the ultraviolet spectrum of 2,6-diacetylpyridine in acetonitrile was recorded. Bands occur at $\sim 35,350$ (~ 2400), $36,500$ (3750), $\sim 37,500$ (~ 3500), and $42,500 \text{ cm}^{-1}$ (7250), and a more intense band occurs beyond $46,000 \text{ cm}^{-1}$. It is informative to note that the first three bands in the zinc complex are all $2900\text{--}2950 \text{ cm}^{-1}$ lower in frequency than the first three bands of diacetylpyridine and have similar relative intensities. The fourth diacetylpyridine band, if present in the condensed macrocycle, would be obscured by the much more intense fourth band of the zinc complex. This similarity between the spectra is not too surprising since the carbonyl

(37) N. F. Curtis and Y. M. Curtis, *J. Chem. Soc., A*, 1912 (1966).

functions of diacetylpyridine have been replaced by the azo-methine functions in the macrocycle and the coordination to zinc probably has less effect on the conjugated system than does coordination to many other metal ions. In the ultraviolet spectra of the cobalt complexes, there tends to be a series of rather vaguely defined shoulders on one or two very intense bands which obscure the lower energy bands observed in the spectrum of the zinc complex.

Experimental Section

Materials.—Anhydrous cobalt(II) bromide and thiocyanate were obtained from City Chemical Co., 2,6-diacetylpyridine was obtained from Aldrich Chemical Co. and Columbia Organic Chemicals, and 3,3'-diaminodipropylamine was obtained from Matheson Coleman and Bell. The diacetylpyridine was recrystallized from hot ethanol before use. Nitrogen was purified before use in the glove box by passing it through a hot tube filled with copper turnings. All other materials were the usual reagent grade.

Physical Measurements.—Visible, near-infrared, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Spectra of solid samples were run on Nujol mulls impregnated on filter paper or with a Cary Model 1411 reflectance attachment, using magnesium carbonate as a blank. For cobalt(II) solution spectra, the solutions were prepared and the quartz cells were filled in a glove box under nitrogen.

A Perkin-Elmer Model 337 recording spectrophotometer was used to obtain all infrared spectra. Infrared spectra were run on potassium bromide pellets and Nujol and hexachlorobutadiene mulls.

Elemental analyses for carbon, hydrogen, and nitrogen were performed in this laboratory, using an F & M Model 185 carbon, hydrogen, and nitrogen analyzer, and by Galbraith Laboratories, Inc. All analyses for other elements were by Galbraith Laboratories, Inc.

The electrical resistances of solutions of the compounds were measured using an Industrial Instruments RC 16B conductivity bridge and a conductance cell with platinum electrodes and a cell constant of 2.116 cm^{-1} . Conductances were determined at 25° at 1000 cps for approximately $10^{-3} M$ solutions.

The magnetic susceptibilities of solid samples were determined by the Gouy method, using $\text{HgCo}(\text{NCS})_4$ as a standard. In the determination of the susceptibilities of cobalt(II) compounds, the Gouy tube was filled in a glove box under nitrogen with dry samples which had never been exposed to oxygen. The calculated moments were the same, within experimental error, as those of samples packed in air after vacuum drying.

A Faraday magnetic susceptibility balance equipped with a Cahn Gram electrobalance and a Varian 4-in. electromagnet fitted with specially shaped pole pieces was used to determine the susceptibility of $\text{Co}(\text{CR})\text{Cl}_2 \cdot \text{H}_2\text{O}$. In this case, an insufficient quantity of the product was available to fill a Gouy tube.

The Gouy balance used to determine magnetic susceptibilities of solutions has been described by Weber.³⁸ The Gouy balance used to determine the temperature dependence has been described by Burke.³⁹ All of the measured susceptibilities were corrected for diamagnetism.⁴⁰ From Pascal's constants a value of -162.7×10^{-6} cgsu was calculated for the magnetic susceptibility of the macrocyclic ligand.

Syntheses.—All reactions involving cobalt(II) were carried out in deoxygenated solvents under nitrogen, unless otherwise stated. Filtrations, volume reductions, and other operations were carried out in a glove box with a nitrogen atmosphere. A small-vacuum desiccator was employed so that solids could be taken into the glove box without introducing oxygen. This

desiccator was also used to remove wet products from the glove box. Following removal from the box, the desiccator was immediately evacuated and the products were dried overnight, over P_4O_{10} . The desiccator, still under vacuum, was then taken back into the glove box and opened. This procedure avoided any exposure to air of the wet and dry samples until the solid-state magnetic susceptibilities had been determined.

2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadecan-1(17),2,11,13,15-pentaenecobalt(II) Bromide Monohydrate, $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$.—This procedure closely followed that of Karn for the preparation of $\text{Ni}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$. Diacetylpyridine (16.3 g, 0.10 mol) was dissolved in 150 ml of hot ethanol. One hundred milliliters of water was added. Cobalt(II) bromide (21.8 g, 0.10 mol) was added and dissolved in the hot mixed solvent. The solution was held at $65\text{--}75^\circ$ and stirred as 3,3'-diaminodipropylamine (13.1 g, 0.10 mol) was added. The solution became cloudy on addition of the amine. Four milliliters of glacial acetic acid was added to clarify the solution. The dark red solution was stirred and heated at $65\text{--}75^\circ$ for 4–6 hr. After removing about half of the ethanol under reduced pressure, the hot solution was filtered. Fifty milliliters of a concentrated solution of lithium bromide in ethanol was added and the solution was set aside to cool to room temperature. The product was collected on a fritted glass funnel and washed with ethanol. This product was recrystallized from hot ethanol with the addition of lithium bromide solution. Black needles of the monohydrate formed and were filtered from the solution, washed with ethanol, and dried *in vacuo* over P_4O_{10} ; yield, 60%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4\text{Br}_2 \cdot \text{H}_2\text{O}$: C, 36.39; H, 4.85; N, 11.32; Br, 32.28. Found: C, 36.60; H, 4.78; N, 11.36; Br, 32.50.

$\text{Co}(\text{CR})(\text{NCS})_2$.—The preparation of this product was similar to that of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ with the following exceptions. Anhydrous cobalt(II) thiocyanate was used instead of cobalt bromide. The product formed as black microcrystalline needles on cooling of the concentrated reaction mixture. This product was not recrystallized as it could be recovered from solution only on long standing and some decomposition occurred; yield, 39%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4(\text{NCS})_2$: C, 47.11; H, 5.11; N, 19.39; S, 14.79. Found: C, 47.31; H, 5.12; N, 19.39; S, 14.95.

$\text{Co}(\text{CR})(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$.—The preparation of this product was similar to that of $\text{Co}(\text{CR})(\text{NCS})_2$ with the exception that cobalt(II) nitrate hexahydrate was used instead of cobalt(II) thiocyanate; yield, 12%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$: C, 40.01; H, 5.15; N, 18.66. Found: C, 40.26; H, 5.13; N, 18.61.

$\text{Co}(\text{CR})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.—The preparation of this product was similar to that of the preceding compounds with the following exception. After heating the reaction mixture for about 4 hr, the solution was concentrated until it became noticeably viscous so as to remove as much ethanol as possible. To this hot solution, a concentrated aqueous solution of sodium perchlorate was added. The product crystallized very rapidly. It was collected, washed thoroughly with ethanol, and dried. Strong heating of the dry compound on a hot plate caused a sharp detonation; yield, 67%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: C, 33.72; H, 4.53; N, 10.49; Co, 11.03; Cl, 13.27. Found: C, 33.9; H, 4.39; N, 10.50; Co, 11.24; Cl, 13.30.

This product was also prepared by dissolving $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ in water and adding aqueous sodium perchlorate. The product was isolated as above; yield, 71%. *Anal.* Found: C, 33.5; H, 4.41; N, 10.5.

$\text{Co}(\text{CR})\text{I}_2$.—One gram of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ was dissolved in 150 ml of warm ethanol. A hot solution of 12 g of sodium iodide in 60 ml of ethanol was added. The color changed from red to brown and small brown-black crystals formed on cooling. The product was collected, washed with ethanol, and dried; yield, 95%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4\text{I}_2$: C, 31.6; H, 3.88; N, 9.81; I, 44.44. Found: C, 31.9; H, 3.68; N, 9.70; I, 44.66.

$\text{Co}(\text{CR})\text{Cl}_2 \cdot \text{H}_2\text{O}$.—A hot saturated solution of lithium chloride in 50 ml of acetone was added to a hot saturated solution of $\text{Co}(\text{CR})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (0.5 g) in acetone. The very finely divided

(38) J. H. Weber, Ph.D. Thesis, The Ohio State University, 1963.

(39) J. Burke, Ph.D. Thesis, The Ohio State University, 1963.

(40) J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960.

product crystallized from the hot solution. The crude product was collected, washed with a small volume of ethanol (in which it is very soluble), and recrystallized from ethanol; yield, 40%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 44.35; H, 5.96; N, 13.79. Found: C, 44.6; H, 6.39; N, 13.5.

Co(CR)py(ClO₄)₂.—To a hot concentrated solution of 1 g of $\text{Co}(\text{CR})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in acetone, a twofold excess of pyridine was added. Upon cooling, small dark maroon crystals formed. The mother liquor was concentrated under reduced pressure to obtain more of the product; yield, 50%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4(\text{C}_5\text{H}_5\text{N})(\text{ClO}_4)_2$: C, 40.3; H, 4.57; N, 11.77. Found: C, 40.4; H, 4.45; N, 11.6.

Co(CR)NH₃(ClO₄)₂.—One gram of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ was dissolved in ethanol and anhydrous ammonia gas was allowed to flow onto the surface of the solution. The color of the solution changed from red to dark maroon. A hot concentrated solution of sodium perchlorate in ethanol was added and the product precipitated immediately. The product was collected in air and washed thoroughly with ethanol in which it is very insoluble; yield, 80%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4(\text{NH}_3)(\text{ClO}_4)_2$: C, 32.7; H, 4.92; N, 12.70; Co, 10.69; Cl, 12.86. Found: C, 33.1; H, 4.62; N, 12.7; Co, 10.84; Cl, 12.94.

Co(CR)Br(ClO₄), Co(CR)Br(PF₆), and Co(CR)BrB(C₆H₅)₄.—A warm concentrated solution of sodium perchlorate in ethanol, ammonium hexafluorophosphate in methanol, or sodium tetrabutylborate in methanol was added to a hot, concentrated solution of $\text{Co}(\text{CR})\text{Br}_2 \cdot \text{H}_2\text{O}$ in the same solvent. A twofold excess of the salt was used. The product crystallized at once as a finely divided black solid; yield, 95%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4\text{BrClO}_4$: C, 36.27; H, 4.46; N, 11.28; Br, 16.09; Cl, 7.14. Found: C, 36.09; H, 4.03; N, 11.42; Br, 15.93; Cl, 7.15. Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4\text{BrPF}_6$: C, 33.22; H, 4.09; N, 10.33; F, 21.02. Found: C, 32.46; H, 4.15; N, 10.15; F, 20.95. Calcd for $\text{CoC}_{15}\text{H}_{22}\text{N}_4\text{BrB}(\text{C}_6\text{H}_5)_4$: C, 65.38; H, 5.97; N, 7.82; Br, 11.15. Found: C, 65.22; H, 6.01; N, 7.84; Br, 11.19.

Zinc(II) Complex, Zn(CR)I₂.—To a solution of 2,6-diacetylpyridine (0.80 g) in 150 ml of 50% ethanol-water, 1.49 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 50 ml of ethanol was added. While holding the temperature of the stirred solution near 70°, 3,3'-diaminodipropylamine (0.63 g) was added, 2–5 drops at a time, over a period of 30 hr. One drop of acetic acid was added occasionally to keep the solution clear. Heating was continued for an additional 15 hr. A large excess of sodium iodide (11 g) in ethanol solution was added and the solution was allowed to cool.

Dark yellow crystals of the crude product formed. This crude product was recrystallized by dissolving it in a minimum volume of warm (60°) dimethylformamide. Five volumes of acetone was added and the solution was cooled in the refrigerator for several days. The bright yellow platelets which formed were collected, washed with acetone, and dried; yield, 10%. *Anal.* Calcd for $\text{ZnC}_{15}\text{H}_{22}\text{N}_4\text{I}_2$: C, 31.2; H, 3.81; N, 9.70; Zn, 11.32; I, 44.95. Found: C, 31.0; H, 3.80; N, 9.69; Zn, 11.37; I, 41.22.

2,12-Dimethyl-3,7,11-tetraazabicyclo[11.3.1]heptadeca-1(17)-13,15-trienecobalt(II) Bromide, Co(CRH)Br₂.—Platinum oxide catalyst was added to a solution of $\text{Co}(\text{CRH})\text{Br}_2 \cdot \text{H}_2\text{O}$ (2.0 g, 0.004 mol) in 200 ml of methanol. This solution was shaken on the Parr hydrogenation apparatus for 4 days. The solution was filtered to remove the catalyst and the volume of the filtrate was reduced until the solution was saturated at 60°. The solution was allowed to cool to room temperature and the reddish brown product was collected. The crude product was recrystallized from ethanol with addition of lithium bromide to induce crystallization. This purified product was collected, washed, and dried *in vacuo* over P_4O_{10} ; yield, 70%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{26}\text{N}_4\text{Br}_2$: C, 37.44; H, 5.44; N, 11.64; Co, 12.24; Br, 33.22. Found: C, 37.35; H, 5.53; N, 11.85; Co, 12.37; Br, 33.29.

Co(CRH)Br(PF₆).—The preparation of this product was similar to that of $\text{Co}(\text{CRH})\text{Br}_2$ with the following exceptions. A methanol solution of NH_4PF_6 was added to the filtrate after removing the catalyst. The bronze crystals which formed are very sparingly soluble in methanol and water; yield, 83%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{26}\text{N}_4\text{BrPF}_6$: C, 33.0; H, 4.80; N, 10.3; Co, 10.79; Br, 14.63. Found: C, 33.2; H, 4.91; N, 10.3; Co, 10.72; Br, 14.62.

Co(CRH)I(PF₆).—The preparation of this product is similar to that of $\text{Co}(\text{CRH})\text{Br}(\text{PF}_6)$ with the following exceptions. $\text{Co}(\text{CR})\text{I}_2$ was used for the hydrogenation. A microcrystalline brown product was obtained; yield, 45%. *Anal.* Calcd for $\text{CoC}_{15}\text{H}_{26}\text{N}_4\text{IPF}_6$: C, 30.37; H, 4.42; N, 9.45; I, 21.39. Found: C, 30.8; H, 4.69; N, 9.42; I, 21.40.

Acknowledgment.—This research was supported (in part) by a Public Health Service fellowship (1-F1-GM-28, 389-01) from the National Institute of General Medical Sciences and by Research Grant GM-10040 from the same institute.

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Perhaloarylmethyl Chemistry. V. The Formation and Properties of Some σ -Perhaloaryl and Methyl Derivatives of Nickel^{1,2}

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Received October 8, 1969

A new series of air-stable, σ -bonded organic derivatives of nickel of the types $[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Ni}(\text{aryl})\text{Cl}$, $[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Ni}(\text{aryl})_2$, and $[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P}]_2\text{Ni}(\text{aryl})\text{CH}_3$ is described. Their proton nmr spectra are consistent with a *trans*-planar configuration in each case. Factors affecting the relative stabilities of these products are discussed.

The chemistry of σ -bonded organonickel compounds has been the subject of an intensive research effort in

(1) Part IV: M. D. Rausch, Y. F. Chang, and H. B. Gordon, *Inorg. Chem.*, **8**, 1355 (1969).

(2) Presented in part at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965, and in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

recent years. These studies have been directed toward the possible utilization of such compounds as homogeneous catalysts, as well as toward a better understanding of the nature of the carbon–nickel σ bond. Chatt and Shaw³ made a major contribution to this

(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).