Inorganica Chimica Acta, *158* (1989) 141–149

Preparation of Tetrakis(2,6-dimethylphenylisocyanide)cobalt(II) Perchlorate in Novel Reactions

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(Received July 20, 1988)

Abstract

Paramagnetic tetrakis(2,6-dimethylphenylisocyanide)cobalt(II) perchlorate, $[Co(CNR)_4](ClO_4)_2$, $R = 2,6\text{-}Me_2C_6H_3$, has been prepared from pentakis(2,6-dimethylphenylisocyanide)cobalt(II) perchlorate hemihydrate, $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$, in novel reactions with triphenylarsine and triphenylstibine. Analogous reaction with $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ produced only $[Co(CNR)_5]BF_4$. Both $[Co(CNR)_5]X_2 \cdot 0.5H_2O$, $X = ClO_4^-$, BF_4^-, can be recrystallized from CH_2Cl_2, $CHCl_3$ or CH_2ClCH_2Cl in 0.15–0.30 M initial concentration, to produce $[Co(CNR)_5]X_2 \cdot S$ (S = adducted solvent) in good yield. Recrystallization of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ from dilute ($C_M \leqslant 5 \times 10^{-3}$ M) solution, however, produces $[Co(CNR)_4](ClO_4)_2 \cdot S$, while $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ regenerates the starting material. Recrystallizations from CH_3CN or CH_3NO_2 produce $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ (concentrated solution) or no recovered product (dilute solution). Solid-state properties of magnetic susceptibilities, diffuse reflectance electronic spectra, and mull-infrared are investigated. Distorted square planar coordination of RNC in $[Co(CNR)_4](ClO_4)_2$ is suggested. Infrared $\nu(ClO_4)$ strongly suggests monodentate ClO_4^- coordination in $[Co(CNR)_4](ClO_4)_2$, or $[Co(CNR)_4(ClO_4)_2]$, while the possibility of weaker ClO_4^- coordination in $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ is ambiguous. Isolation of $[Co(CNR)_4](ClO_4)_2$ is the first observed incident of significant difference between BF_4^- and ClO_4^- salts of Co(II)–arylisocyanide complexes.

Introduction

Five-coordination is the preferred stoichiometry in reactions of arylisocyanides with cobalt(II) salts of non-coordinating anions. Pentakis(arylisocyanide)-cobalt(II) complexes are reported here: anhydrous and/or hydrated $[Co(CNR)_5]X_2 \cdot nH_2O$, where $X = ClO_4^-$ or BF_4^-; and $R = C_6H_5$, $o\text{-}MeC_6H_4$, $p\text{-}MeC_6H_4$, $p\text{-}FC_6H_4$, $o\text{-}EtC_6H_4$, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Et_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$. These compounds were prepared by reaction of stoichiometric or excess RNC with $CoX_2 \cdot 6H_2O$ [1–6]. Reaction of the nitrate and acetate salts [3, 5] or the *p*-halophenylisocyanides [7] causes spontaneous reduction to Co(I). Methylisocyanide and ethylisocyanide are known to form metal–metal bonded dimers, $[(RNC)_5Co{-}Co(CNR)_5](ClO_4)_4$, R = Me, Et [8, 9]; while monomeric $[Co(CNMe)_5](ClO_4)_2$ has been reported [1, 3, 10] but not reproduced [4]. Only t-butylisocyanide appears to form a tetrakis(alkylisocyanide) complex, $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, upon initial reaction with $Co(ClO_4)_2 \cdot 6H_2O$ [11].

Tetrakis- and bis(organoisocyanide)cobalt(II) complexes, however, can be prepared with coordinating anions. The 'diisocyanide' derivatives, $CoX_2(CNMe)_2$, X = Cl, Br, SCN [3, 5, 10, 12], are recognized [13, 14] as having structures, $[Co(CNMe)_4][CoX_4]$, similar to $[Co(CNMe)_4]CdX_4$ ($X = Br^-$, I^- [14]), with X-ligand bridging between anionic and cation complexes. Paramagnetism of 1.82 BM is assumed for $[Co(CNMe)_4]^{2+}$. Other 'diisocyanide' complexes, $CoCl_2(CNEt)_2$, $CoBr_2(CNC_6H_5)_2$ and $Co(SCN)_2(CNR)_2$, $R = C_6H_5$, $C_6H_4Me\text{-}p$, $C_6H_4OMe\text{-}p$ [3, 5], may have analogous structures. Numerous 'tetraisocyanide' derivatives have also been reported: $CoX_2(CNR)_4$, where $X = Cl^-$ and R = Me or C_6H_5; $X = Br^-$ and R = Me, C_6H_5, or $C_6H_4Me\text{-}p$; $X = I^-$ and R = Me, C_6H_5, $C_6H_4OMe\text{-}p$, $C_6H_4Cl\text{-}p$, $C_6H_4Cl\text{-}m$, $C_6H_3Me_2\text{-}2,4$, $C_6H_3Me\text{-}2,Cl\text{-}3$, $C_6H_3Me\text{-}2,Cl\text{-}4$, $C_6H_3Cl_2\text{-}2,5$, $C_{10}H_7$ [3, 5, 14, 15]; and $K_4[CoBr_2(CNC_6H_4SO_3\text{-}p)_4]$, and $Co_2[CoX_2(CNC_6H_4CO_2\text{-}p)_4]$ where $X = Br^-$, I^- [3, 5]. The iodide complexes provide the best candidates for investigation since many exist in both diamagnetic (α) and one-electron paramagnetic (β) forms with interconversions possible. The β complexes are formulated as $[Co(CNR)_4]I_2$, while the α structure could be $[Co_2I_2(CNR)_8]I_2$ [3, 5].

Single crystal X-ray diffraction of $Co(CNC_6H_4Me\text{-}p)_4I_2$ (β complex), for example, has established that the complex is approximately pseudo-octahedral

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trans-[Co(CNC$_6$H$_4$Me-*p*)$_4$I$_2$] [16]. Deliberate attempt was made to prepare tetrakis complexes with non-bridging, non-coordinating anions such as ClO$_4^-$ and BPh$_4^-$, and the conclusion was reached that anion ability to bridge into the pseudo-octahedral coordination sites was necessary to stabilize [Co(CNMe)$_4$]$^{2+}$ in the solid state [14].

Reaction of tertiary phosphorus ligands in 5:1 mole ratio with organoisocyanidecobalt(II) complexes causes ligand substitution/reduction. Triarylphosphines and trialkylphosphites exclusively disubstitute with pentakis(arylisocyanide)cobalt(II), [Co(CNR)$_3$L$_2$]X, L = P(C$_6$H$_5$)$_3$, P(C$_6$H$_4$Cl-*p*)$_3$, P(C$_6$H$_4$OMe-*p*)$_3$, P(OMe)$_3$, or P(OEt)$_3$, and X = ClO$_4^-$ or BF$_4^-$ [17–19]. Triarylphosphites and trialkylphosphines, on the other hand, where L = P(OC$_6$H$_5$)$_3$, P(OC$_6$H$_4$Cl-*p*)$_3$, P(C$_6$H$_{13}$-n)$_3$, P(C$_2$H$_4$CN)$_3$, or P(NEt$_2$)$_3$, undergo both monosubstitution and disubstitution, depending upon the arylisocyanide and/or phosphorus ligand [17, 20]. Triarylphosphines and trialkylphosphines disubstitute in [Co(CNCMe$_3$)$_4$H$_2$O](ClO$_4$)$_2$, yielding [Co(CNCMe$_3$)$_3$(PR$_3$)$_2$]ClO$_4$ [11]. The complex [Co(CNC$_6$H$_5$)$_3${As(C$_6$H$_5$)$_3$}$_2$]ClO$_4$ has been prepared by analogous reaction of As(C$_6$H$_5$)$_3$ with [Co(CNC$_6$H$_5$)$_5$](ClO$_4$)$_2$·1.0H$_2$O [21]. Reaction with [Co(CNC$_6$H$_3$Me$_2$-2,6)$_5$](ClO$_4$)$_2$·0.5H$_2$O could have been expected to be similar.

Experimental

RNHCHO (hereafter, R = C$_6$H$_3$Me$_2$-2,6) was prepared from commercial RNH$_2$ (Aldrich) and formic acid [22]. Anhydrous diethyl ether was filtered through an alumina column immediately before use. IR spectra were recorded on a Perkin-Elmer 1710 Infrared Fourier Transform spectrophotometer in nujol mulls and in solution using a single NaCl cell. Electronic spectra were recorded on a Cary 2390 with an integrating sphere diffuse reflectance attachment; absorbance values reported are *versus* BaSO$_4$ standard. Melting (decomposition) ranges were measured in capillaries using an Electrothermal melting point apparatus. Magnetic susceptibilities (Gouy method) were measured at ambient temperatures using a five-place Mettler electrobalance and an electromagnet operated at a field of 10.0 KG. Pyrex Gouy tubes were calibrated with Hg[Co(SNC)$_4$] according to standard procedures [23]; the Hg[Co(SCN)$_4$] was prepared from CoSO$_4$·7H$_2$O by established methods [24]. Effective magnetic moments were calculated according to the assumed Curie law behavior, $\mu_{\mathrm{eff}} = 2.84\sqrt{X'_{\mathrm{M}}T}$ BM, $X'_{\mathrm{M}} = X$(uncorrected) × formula weight + diamagnetic corrections. Diamagnetic corrections were approximated from literature values and calculations using Pascal's constants [23, 25]. Elemental analyses were performed commercially.

Preparation of [Co(CNC$_6$H$_3$Me$_2$-2,6)$_5$](ClO$_4$)$_2$·0.5H$_2$O

The RNC was prepared from 2,6-dimethylphenylformamide and *p*-toluenesulfonyl chloride in triethylamine by modification [26] of the synthesis by Hertler and Corey [27], and purified by vacuum sublimation (41% yield). A solution of 2.28 g RNC dissolved in 33.0 ml EtOH was added dropwise to a filtered, well-stirred solution of 1.26 g Co(ClO$_4$)$_2$·6H$_2$O dissolved in 15.0 ml EtOH in an ice bath. The dark green microcrystals were filtered from a golden yellow filtrate as soon as addition was complete, and air dried under suction. Yield: 2.97 g (93%). Melting (decomposition) range: slow decomposition above 210 °C, violent decomposition at 235–240 °C. IR: ν(–N≡C), 2204s, ~2194sh, ~2233vw(sh) cm^{-1} (nujol). Electronic spectrum (diffuse reflectance): ~733br (A = 1.65), ~358br (1.70), ~325sh (1.67), 287(1.62), ~268sh (1.56), 226 (1.44) nm. Magnetic susceptibility: μ_{eff} = 1.9 BM ($X_{\mathrm{M}} = 1070 \times 10^{-6}$). *Anal.* Calc. for CoC$_{45}H_{45}Cl_2N_5O_8$·0.5H$_2$O: C, 58.58; H, 5.03; N, 7.59; Cl, 7.68. Found: C, 58.58; H, 4.93; N, 7.36; Cl, 7.80%. Calc. for CoC$_{45}$H$_{45}$Cl$_2$N$_5$O$_8$: C, 59.15; H, 4.96; N, 7.66; Cl, 7.76%.

Analogous preparation of [Co(CNR)$_5$](BF$_4$)$_2$·0.5H$_2$O: yellow–green microcrystals, 94% yield. Melting (decomposition) range: 175–195 °C, slow decomposition. IR: ν(–N≡C), 2207s, 2199sh, ~2237w(sh) cm^{-1} (nujol). Electronic spectrum: ~745br (A = 1.38), 468 (0.86), ~403sh (1.23), ~322br (1.62, ~282sh (1.58), ~260sh (1.50), 225 (1.46) nm. Magnetic susceptibility: μ_{eff} = 2.0 BM ($X_{\mathrm{M}} = 1180 \times 10^{-6}$). *Anal.* Calc. for CoC$_{45}H_{45}B_2F_8N_5$·0.5H$_2$O: C, 60.23; H, 5.17; N, 7.80. Found: C, 60.01; H, 5.05; N, 7.76%. Calc. for CoC$_{45}$H$_{45}$B$_2$F$_8$N$_5$: C, 60.84; H, 5.11; N, 7.88%.

Preparation of [Co(CNC$_6$H$_3$Me$_2$-2,6)$_4$](ClO$_4$)$_2$

A 1.000 g sample of [Co(CNC$_6$H$_3$Me$_2$-2,6)$_5$](ClO$_4$)$_2$·0.5H$_2$O was dissolved in 3.5 ml CH$_2$Cl$_2$, filtered through cotton, and chilled in ice. Then, 1.66 g As(C$_6$H$_5$)$_3$ (5:1 mole ratio) in 1.0 ml CH$_2$Cl$_2$ was added dropwise with swirling at 0 °C. The dark green solution turned opaque yellow–brown during ligand addition; only faint odor of RNC was noted. The solution was allowed to stand 45 min at 25 °C, then filtered through cotton. The addition of 4.5 ml ether dropwise effected initial precipitation. A total volume of 10.0 ml ether was added, the solution was chilled in ice for 30 min, and a pale orange solid was filtered from wine-colored filtrate and dried under suction/air. Crude product (262 mg, 31% yield) was dissolved in 4.0 ml CH$_2$Cl$_2$ and filtered through cotton to produce a clear, greenish-yellow solution. Addition of 4.0 ml ether dropwise and chilling in ice for 50 min produced granular, pale orange crystals which were filtered from yellow–brown solution and dried under suction/air. Yield: 215 mg (25%). Melting (decomposition) range: 240–245 °C (uncorrected) with decomposition. IR: $\nu(-N\equiv C)$, 2204s, ~2170w(sh) cm^{-1} (nujol). Electronic spectrum: ~919br ($A = 0.92$), 459 (0.91), ~353br (1.63), ~365sh (1.57), 275 (1.63), 224 (1.40) nm. Magnetic susceptibility: $\mu_{eff} = 2.0$ BM ($X_M = 1250 \times 10^{-6}$). *Anal.* Calc. for $CoC_{36}H_{36}Cl_2N_4O_8$: C, 55.26; H, 4.64; N, 7.16; Cl, 9.06. Found: C, 55.56; H, 4.85; N, 7.14; Cl, 9.11%.

The analogous reaction of $Sb(C_6H_5)_3$ with $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ in 5:1 mole ratio was carried out at 0 and 25 °C. Reaction at 0 °C failed to show a color change during ligand addition, but solution color slowly changed from emerald green to yellow–green during the 30 min reaction period at room temperature, and to a light yellow when sufficient ether was then added to effect precipitation. Yield: 23% (recrystallized from CH_2Cl_2/ether). IR: $\nu(-N\equiv C)$, 2204s, ~2170w(sh) cm^{-1} (nujol). A second crop of $[Co(CNR)_5]ClO_4 \cdot CH_2Cl_2$ (19%) was recovered upon addition of excess ether to the filtrate and extensive refrigeration. $\nu(-N\equiv C)$: 2185w, 2138s, 2123s, 2112s, 2081vs cm^{-1} (nujol). Reaction at 25 °C gave immediate color change to yellow–green during ligand addition, but a lower yield of recrystallized product (16%) because of contamination with $[Co(CNR)_5]ClO_4$ in the first as well as second crop.

Analogous reaction of $As(C_6H_5)_3$ with $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ in 5:1 mole ratio at 0 °C was attempted and significant differences were observed. The initially dark green solution turned red–brown (bromine red) during ligand addition, with noticeable RNC odor. Considerably more ether was required to precipitate first and second crops of pale yellow solid. Upon recrystallization from CH_2Cl_2/ether, a white first crop (discarded) was invariably obtained, while a second crop of $[Co(CNR)_5]BF_4 \cdot CH_2Cl_2$ was recovered with difficulty. Yield: 24%. IR: $\nu(-N\equiv C)$, 2142s, 2100vs cm^{-1} (nujol); 2140s, 2105vs cm^{-1} (CH_2Cl_2). Electronic spectrum: 326br ($\epsilon \sim 35\,000$), ~288sh, 255 (70 000) nm (CH_2Cl_2 solution).

Recrystallization of $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2 \cdot 0.5H_2O$

A 0.30 M solution was prepared by dissolving 255 mg $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ in 1.0 ml CH_2Cl_2 and filtering through cotton. (A saturated solution is about 0.5 M.) Ether was added dropwise to this emerald green solution, with initial precipitation occurring at 1.0 ml. A total of 3.0 ml ether was added, and the solution chilled 45 min in ice, then blue–green crystals were filtered from the golden yellow solution. Upon thorough drying under suction/air, the product became dull dark green. Throughout this procedure, a chocolate brown residue with strong odor of RNC formed wherever solution evaporated, but was avoided in the final product. Yield: 251 mg (85% recovery, based on $[Co(CNR)_5](ClO_4)_2 \cdot CH_2Cl_2$). IR: $\nu(-N\equiv C)$, 2204s, ~2195m(sh), ~2233vw(sh) cm^{-1} (nujol). Electronic spectrum: ~735br ($A = 1.18$), ~412sh (1.07), ~326br (1.51), ~282sh (1.56), 262 (1.64), 215 (1.51) nm. *Anal.* Calc. for $CoC_{45}H_{45}Cl_2N_5O_8 \cdot 0.3CH_2Cl_2$: C, 57.93; H, 4.89; N, 7.46. Found: C, 57.92; H, 4.84; N, 7.25%.

Analogous recrystallization of $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ from CH_2Cl_2/ether gave a 64% yield based on $[Co(CNR)_5](BF_4)_2 \cdot CH_2Cl_2$. IR: $\nu(-N\equiv C)$, 2205s, ~2199m(sh), ~2236w(sh) cm^{-1} (nujol). Electronic spectrum: ~743br ($A = 1.30$), 452 (1.08), ~324br (1.56), ~279br (1.57), 223 (1.42) nm.

Recrystallization of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ from CH_2ClCH_2Cl/ether was accomplished by dissolving 270 mg in 2.0 ml CH_2ClCH_2Cl (~0.15 M) giving a dark yellow green solution after filtration through cotton. An initial pale orange precipitate was formed upon addition of 2.0 ml ether. The solid became dark green upon continued addition of ether (total volume of added ether was 5.0 ml). Dark green microcrystals were recovered from a yellow filtrate with a small amount of chocolate brown residue remaining where the solution had evaporated. Yield: 220 mg (74% based on $[Co(CNR)_5](ClO_4)_2 \cdot CH_2ClCH_2Cl$). IR: $\nu(-N\equiv C)$, 2203s, ~2197s(sh), ~2168vw(sh), ~2225vw(sh) cm^{-1} (nujol). *Anal.* Calc. for $CoC_{45}H_{45}Cl_2N_5O_8 \cdot 0.25CH_2ClCH_2Cl$: C, 58.23; H, 4.94; N, 7.46. Found: C, 58.22; H, 4.86; N, 7.30%.

The analogous recrystallization of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ from $CHCl_3$/ether gave a 75% yield. IR: $\nu(-N\equiv C)$, 2203s, ~2192m(sh), ~2171w(sh) cm^{-1} (nujol). *Anal.* Calc. for $CoC_{45}H_{45}Cl_2N_5O_8 \cdot 0.6CHCl_3$: C, 55.58; H, 4.66; N, 7.11. Found: C, 55.74; H, 4.68; N, 6.93%.

Recrystallization of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ from CH_3CN/ether: 280 mg was dissolved in 2.0 ml CH_3CN (~0.15 M) giving a dark green solution after filtration through cotton. There was an initial precipitate of blue solid when 5.0 ml ether was added. The total volume of added ether was 7.0 ml. Dark blue microcrystals were separated from a yellow filtrate and dried to a dull blue–green under suction/air. Yield: 216 mg (77% based on $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$). IR: $\nu(-N\equiv C)$, 2204s, ~2194m(sh), ~2231vw(sh) cm^{-1} (nujol). *Anal.* Calc. for $CoC_{45}H_{45}Cl_2N_5O_8 \cdot 0.5H_2O$: C, 58.58; H, 5.02; N, 7.59. Found: C, 58.44; H, 4.90; N, 7.31%.

An analogous recrystallization of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ from CH_3NO_2/ether gave a 76% recovery with $\nu(-N\equiv C)$, 2205s, 2192m, ~2234vw(sh) cm^{-1} (nujol).

Alternate Preparation of $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$

A 5.0×10^{-3} M solution was prepared by dissolving 115 mg of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ in 25.0 ml CH_2Cl_2. Ether was slowly added to this emerald green solution. After addition of 65.0 ml ether, and with scratching the flask walls, a pale orange solid began to form and the solution color became noticeably more yellow. Odor of RNC was evident. A total of 80.0 ml ether was added and the solution chilled thoroughly (~2 h) before the pale orange microcrystals were filtered from greenish-yellow solution. Yield: 91 mg (85% based on $[Co(CNR)_4](ClO_4)_2\cdot CH_2Cl_2$). IR: ν(−N≡C), 2204s, ~2170w(sh) cm^{-1} (nujol). *Anal.* Calc. for $CoC_{36}H_{36}Cl_2N_4O_8\cdot 0.2CH_2Cl_2$: C, 54.38; H, 4.59; N, 7.01; Cl, 10.64. Found: C, 54.56; H, 4.61; N, 7.04; Cl, 10.64%.

Analogous recrystallization of 5.0×10^{-3} M $[Co(CNR)_5](ClO_4)_2\cdot 0.5H_2O$ in $CHCl_3$ (119 mg/25.0 ml) was accomplished by precipitation with 30.0 ml added ether (total volume of ether used was 40.0 ml). Yield: 85.5 mg (74% based on $[Co(CNR)_4](ClO_4)_2\cdot CHCl_3$). IR: ν(−N≡C), 2204s, ~2192vw(sh), ~2170w(sh) cm^{-1} (nujol). *Anal.* Calc. for $CoC_{36}H_{36}Cl_2N_4O_8\cdot 0.42CHCl_3$: C, 52.53; H, 4.41; N, 6.73. Found: C, 52.54; H, 4.60; N, 6.73%.

Analogous recrystallization of 5.0×10^{-3} M $[Co(CNR)_5](ClO_4)_2\cdot 0.5H_2O$ in CH_2ClCH_2Cl (120 mg/25.0 ml): initial precipitation by 50.0 ml added ether, with a total volume of 75.0 ml ether used. Yield: 68 mg (60% based on $[Co(CNR)_4](ClO_4)_2\cdot CH_2ClCH_2Cl$). IR: ν(−N≡C), 2204s, ~2170w(sh) cm^{-1} (nujol). *Anal.* Calc. for $CoC_{36}H_{36}Cl_2N_4O_8\cdot 0.75CH_2ClCH_2Cl$: C, 52.57; H, 4.59; N, 6.54. Found: C, 52.30; H, 4.54; N, 6.78%.

An attempted recrystallization of 5.0×10^{-3} M $[Co(CNR)_5](ClO_4)_2\cdot 0.5H_2O$ in CH_3CN (126 mg/25.0 ml) failed to yield crystalline product. The solution remained green with no precipitation to 100 ml added ether, and slowly turned bright yellow (reduction to $[Co(CNR)_5]ClO_4$) over a period of several days. Similar results were seen in the attempted recrystallization of 5.0×10^{-3} M $[Co(CNR)_5](ClO_4)_2\cdot 0.5H_2O$ in CH_3NO_2.

Recrystallization of 5.0×10^{-3} M $[Co(CNR)_5](BF_4)_2\cdot 0.5H_2O$ in CH_2Cl_2 (45 mg/10.0 ml) required initial filtration through cotton and 30.0 ml ether before precipitation of a pale yellow–green solid. Total volume of 40.0 ml ether was used. Yield: 26 mg (58% based on $[Co(CNR)_5](BF_4)_2\cdot 0.5H_2O$). IR: ν(−N≡C), 2209s, 2197m, ~2238w(sh) cm^{-1} (nujol). The analogous recrystallization of 5.0×10^{-3} M $[Co(CNR)_5](BF_4)_2\cdot 0.5H_2O$ in $CHCl_3$ (46 mg/10.0 ml) required initial filtration through cotton and 25.0 ml ether for precipitation of dark green solid. Yield: 17 mg (33% based on $[Co(CNR)_5](BF_4)_2\cdot CHCl_3$). IR: ν(−N≡C), 2205s, ~2199w(sh), ~2235w(sh) cm^{-1} (nujol).

Preparation of $[Co(CNC_6H_3Me_2\text{-}2,6)_5]ClO_4$

An 800 mg sample of $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2\cdot 0.5H_2O$ was dissolved in 4.0 ml pyridine, the initially dark green solution becoming dark orange with gelatinous suspension within several minutes at room temperature. A yellow–white residue was removed by filtration and distilled water was slowly added dropwise. Initial precipitation was observed after addition of 2.0 ml water. Total volume of 5.0 ml water was added, the solution chilled thoroughly (~1 h), and golden yellow granular crystals were filtered and dried under suction/air. Crude product (595 mg) was dissolved in 1.5 ml $CHCl_3$, filtered through cotton, and precipitated by dropwise addition of 5.5 ml ether. Yield: 575 mg (71% based on $[Co(CNR)_5]ClO_4\cdot CHCl_3$). IR: ν(−N≡C), 2088vs(br), 2137s, ~1994vw(sh) cm^{-1} (nujol). The sample was subsequently recrystallized from CH_2Cl_2/ether with ν(−N≡C), 2080vs, 2112s, 2123s, 2138s, 2185w cm^{-1} (nujol) and 2105vs, 2140s cm^{-1} (CH_2Cl_2 solution). Electronic spectrum: 326br ($\epsilon \sim 36000$), ~288sh, 258 (72000) nm in CH_2Cl_2 solution; 325br ($\epsilon \sim 31000$), ~287sh, 257 (64000) nm in $CHCl_3$ solution; and 324br ($\epsilon \sim 19000$), ~283sh, 255 (44000), 236sh (54000) nm in CH_3CN solution. *Anal.* Calc. for $CoC_{45}H_{45}ClN_5O_4\cdot 0.65CH_2Cl_2$: C, 63.06; H, 5.37; N, 8.05. Found: C, 62.94; H, 5.44; N, 8.18%.

Results and Discussion

Syntheses of the Complexes

Preparation of the starting compounds $[Co(CNR)_5](ClO_4)_2\cdot 0.5H_2O$ and $[Co(CNR)_5](BF_4)_2\cdot 0.5H_2O$ was analogous to previous reactions of arylisocyanides with Co(II) [2–7, 17, 26, 28, 29], except that minimum ethanol was used to dissolve the cobalt salt in order to compensate for the limited solubility of the solid RNC. Extent of hydration may be humidity and/or age dependent. The $[Co(CNR)_5](ClO_4)_2\cdot 0.5H_2O$ has sometimes been prepared as dark blue microcrystals that became dark green upon prolonged exposure to the atmosphere, and the (nujol) ν(O–H) at ~3360 and ~3455 cm^{-1} are weaker or absent in some samples. In general, the ν(O–H) bands for the hydrated complexes tend to be weak, making the interconversion of chlorohydrocarbon adduct to hydrate difficult to follow. Change in ν(−N≡C) pattern, but not necessarily frequencies, is more reliable in distinguishing hydrate and adduct. Although resolution is usually still incomplete, the hydrates tend to show more distinct separation of the three (−N≡C) IR bands. This criterion distinguished $[Co(CNR)_5](BF_4)_2\cdot 0.5H_2O$ from $[Co(CNR)_5](BF_4)_2\cdot CHCl_3$ in the crystallization of 5.0×10^{-3} M solutions in CH_2Cl_2 and $CHCl_3$, respectively. Recrystallization of $[Co(CNR)_5]X_2\cdot 0.5H_2O$, $X = ClO_4^-$, BF_4^-, in concentrated solution removes the (weakly-coordinated) H_2O and introduces (adducted) solvent molecules, except with CH_3CN and CH_3NO_2. These solvent–adduct complexes eventually rehydrate after or during total loss of chlorohydrocarbon, albeit slowly. The $[Co(CNR)_4](ClO_4)_2$, however, does not appear to become hydrated after loss of adducted chlorohydrocarbon solvent, since there is no evidence from elemental analyses nor changes in IR spectrum.

Conversion of $[Co(CNR)_5](ClO_4)_2$ to $[Co(CNR)_4](ClO_4)_2$ through recrystallization from dilute chlorohydrocarbon solution appears to be effective only for concentrations $\leq 5 \times 10^{-3}$ M, although equilibrium is observed already at 0.15 M. Recrystallization of 0.1 M $[Co(CNR)_5](ClO_4)_2$ in CH_2Cl_2 gave an orange–green mixed first crop, and dark green second crop. If enough ether is added initially to cause precipitation as one crop, only the green ('pentakis') complex will be isolated. The $[Co(CNR)_4](ClO_4)_2$ is less soluble in, and considerably easier to precipitate from, CH_2Cl_2 than is $[Co(CNR)_5](ClO_4)_2$. Recrystallization of 1.0×10^{-2} M $[Co(CNR)_5](ClO_4)_2$ in CH_2Cl_2 produced an initial pale orange solid, which became an orange–green mixture as precipitation was completed, and converted to dark green $[Co(CNR)_5](ClO_4)_2 \cdot CH_2Cl_2$ upon prolonged refrigeration. Precipitation from 3.0×10^{-3} M $[Co(CNR)_5](ClO_4)_2$ in CH_2Cl_2 produced pale orange $[Co(CNR)_4](ClO_4)_2 \cdot CH_2Cl_2$, but required excess volume of ether. Failure to recover crystalline product from 5.0×10^{-3} M $[Co(CNR)_5](ClO_4)_2$ in CH_3CN and CH_3NO_2 may only reflect the greater difficulty of precipitating $[Co(CNR)_5](ClO_4)_2$ and $[Co(CNR)_4](ClO_4)_2$ in these solvents (but not necessarily their greater solubility) as compared to CH_2Cl_2, $CHCl_3$ and CH_2ClCH_2Cl. (The solvents CH_3OH, $CH_3C(O)CH_3$, Me_2NCHO and Me_2SO cause reduction to Co(I), and solubility is low in Cl_3CCH_3 and tetrahydrofuran.) Formation of the chlorohydrocarbon solvent adducts probably facilitates isolation of the 'tetrakis' complex, but whether these solvents assist in the necessary loss of the one RNC better than solvents not forming adducts is uncertain. No direct coordination to the Co(I) is assumed for adducted chlorohydrocarbon molecules. Why $[Co(CNR)_5](BF_4)_2$ fails to undergo analogous transformation is also uncertain, but inability to form comparably-stable chlorohydrocarbon adducts cannot be the reason.

Reaction of triphenylarsine and triphenylstibine to deplete RNC, or react in some other way, to effect conversion of $[Co(CNR)_5](ClO_4)_2$ into $[Co(CNR)_4](ClO_4)_2$ was unexpected and is currently without adequate explanation. Preparation of $[Co(CNR)_3(AsPh_3)_2]ClO_4$ [17, 21], or simple reduction to $[Co(CNR)_5]ClO_4$, was the expected result. The $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ reacted more as expected. Color change to intense bromine red and odor of liberated RNC during ligand addition characterize reduction/ligand-substitution reactions [17, 21], so transient $[Co(CNR)_3(AsPh_3)_2]BF_4$ may have been prepared in solution. Even $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ has limited solution and solid-state stability [21, 30], however, so any $[Co(CNR)_3(AsPh_3)_2]BF_4$ formed could easily revert to stable $[Co(CNR)_5]BF_4$ in the presence of excess RNC. In the triphenylarsine and triphenylstibine reactions with $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$, reduction to Co(I) presumably does not occur directly upon ligand addition, but takes place as Co(II) remains in solution. Shortening reaction time from 45 min to 5 min in the triphenylarsine reaction, however, has not improved yield of $[Co(CNR)_4](ClO_4)_2$. $[Co(CNR)_5]ClO_4$ has also not been isolated in the triphenylarsine reactions, although it is probably present as an unrecovered second crop. ($[Co(CNR)_5]ClO_4$ is highly soluble in CH_2Cl_2.) Since the effective concentration of $[Co(CNR)_5](ClO_4)_2$ is ~0.24 M, this is not a recrystallization from dilute solution, and the triphenylarsine or triphenylstibine must participate in the reaction, although their role is not clear. The preparation of $[Co(CNR)_4](ClO_4)_2$, but no evidence for the formation of the analogous tetrafluoroborate salt, is the first reaction in which a significant difference in behavior has been observed for ClO_4^- and BF_4^- salts of Co(II) or Co(I) complexes with organoisocyanide ligands. In their Co(I) chemistry, the two salts are extremely similar.

Chocolate brown residues, or in some instances whole samples, have often been observed in Co(II) reactions with a number of different arylisocyanides. It has been assumed to indicate partial decomposition of the complex since odor of liberated RNC is very strong. The residue is most easily observed by rapid evaporation of solutions, especially on ground glass or paper surfaces. This, however, is not a practical method for preparing sizeable amounts. Chocolate brown to dark grey solids, which may be the same material, are prepared by the reaction of poor quality RNC. Samples of this material have been fractionally recrystallized (CH_2Cl_2/ether) into $[Co(CNR)_4](ClO_4)_2$ (13% yield) and an unidentified intense blue–black solid, which may be purely organic. The chocolate brown materials are reduced to $[Co(CNR)_5]ClO_4$ by C_5H_5N in variable yields. Arylisocyanides are intrinsically unstable molecules, slowly decomposing spontaneously (presumably through polymerization) and acting as reducing agents toward a number of transition metal cations (including Co(II)), so partial solution decomposition of these complexes should not be unexpected. Decomposition materials are intensely colored, so a possibly minor constituent could impart its color to a bulk sample.

Preparation of $[Co(CNR)_5]ClO_4$ through pyridine-reduction of $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ establishes that Co(II) primarily reduces rather than disproportionates. Recovery of recrystallized $[Co(CNR)_5]ClO_4 \cdot CHCl_3$ in greater than 70% yield excludes the possibility of extensive Co(III) formation. Behavior of the Co(II) complexes had initially suggested the possibility of a disproportionation equilibrium, but with no direct evidence for a Co(III) species, simple reduction to Co(I) must be occurring.

Characterization in the Solid State

Physical properties of melting (decomposition) ranges, $\nu(-N\equiv C)$ (nujol), diffuse reflectance electronic spectra, and magnetic susceptibilities/effective magnetic moments are reported with preparation of the respective complexes above. The perchlorate salts exhibit violent decomposition at the final state of heating, unlike the Co(I) perchlorates previously characterized [7, 17–21, 26, 29–32], so many decomposition temperatures were omitted. Large diamagnetic corrections and the constants (α, β, δ) for the Gouy tubes used caused relatively small, negative in-field weight measurements (*i.e.* F_{ave}, where $F' = F_{ave} - \delta$, $10^6X = (\alpha + \beta F')/$(sample weight)), which lead to lower precision than could have been expected from this electromagnetic field strength. The effective magnetic moments reported, therefore, should be understood to indicate one-electron paramagnetism, but are not sufficiently accurate to allow further interpretation.

Structures of the complexes in the solid state are probably tetragonal in all cases. The $\nu(-N\equiv C)$ patterns for $[Co(CNR)_4](ClO_4)_2$, $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ and $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ are shown in Fig. 1. The major band is at the same frequency (2204 cm^{-1}) in both ClO_4^- salts and very similar (2207 cm^{-1}) in the BF_4^- salt. The $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$, and presumably also the corresponding BF_4^- salt, appears analogous to $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot nH_2O$ ($n = 1.0, 1.5$), which has been interpreted as pseudo-octahedral, with square pyramidal coordination of C_6H_5NC, as also for $[Co(CNC_6H_5)_5](ClO_4)_2$ (yellow form) [4, 33]. Three allowed $\nu(-N\equiv C)$ bands are expected for C_{4v} symmetry (*i.e.* $2A_1 + E$). The structure of $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot 0.5CH_2ClCH_2Cl$ has been established as square pyramidal by single-crystal X-ray diffraction [34]. The observed change in the $\nu(-N\equiv C)$ pattern from hydrate to chlorohydrocarbon adduct could be explained if the apical-to-basal bond angle increased to an energetically more favorable value of ~100–103° [35] in the adduct complexes from values necessarily more closely approximating 90° in the pseudo-octahedral hydrates. Symmetry could remain C_{4v}, but $\nu(-N\equiv C)$ (especially in nujol mull) would become less distinguishable. One-electron paramagnetism is expected for square pyramidal coordination of Co(II) with the strong-field RNC ligands.

$[Co(CNR)_4](ClO_4)_2$ in the solid state is best explained as distorted square planar coordination, on the basis of available data. Two allowed $\nu(-N\equiv C)$ are compatible with C_{4v} (*i.e.* $A_1 + E$) or D_{2d} ($B_2 + E$) symmetry, but not strict D_{4h} (only E_u) or T_d (only T_2). One electron paramagnetism excludes tetrahedral coordination, and a metal–metal bonded dimeric complex, $[(RNC)_4Co-Co(CNR)_4](ClO_4)_4$, would be expected to be diamagnetic [8, 9]. The RNC ligands in $[Co(CNC_6H_4Me\text{-}p)_4I_2]$ (overall S_4 molecular symmetry) are in a D_{2d} arrangement about Co(II), with rather long (*i.e.* weak) Co–I bonds [16]. Possibly an analogous arrangement exists in $[Co(CNR)_4](ClO_4)_2$.

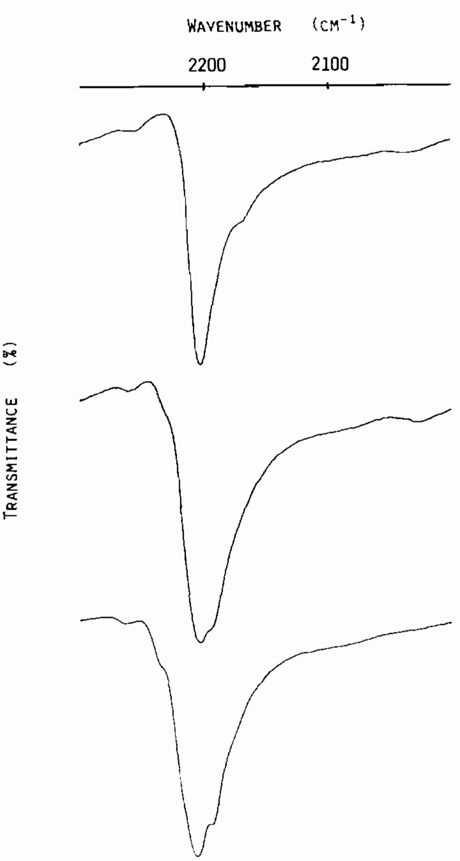

Fig. 1. The $\nu(-N\equiv C)$ pattern (nujol/NaCl, 2300–2000 cm^{-1}) for $[Co(CNR)_4](ClO_4)_2$, $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$, and $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ (top to bottom, respectively), where $R = 2,6\text{-}Me_2C_6H_3$.

Diffuse reflectance electronic spectra were measured on the five types of complexes: $[Co(CNR)_4](ClO_4)_2$, and the hydrates and chlorohydrocarbon adducts of $[Co(CNR)_5](ClO_4)_2$ and $[Co(CNR)_5](BF_4)_2$. Spectra of $[Co(CNR)_4](ClO_4)_2$ and $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ are shown in Fig. 2. There are really only two different spectral types: $[Co(CNR)_4](ClO_4)_2$ and the 'pentakis' complexes, which are similar. The chlorohydrocarbon adducts show more detail in the UV region than the corresponding hydrates, and the BF_4^- salts show resolution of a band at ~450–470 nm that is unresolved in the ClO_4^- salts, but basically these four spectra are the same. The first band is so broad that considerable error exists in reading λ_{max}. By analogy with spectra for the C_6H_5NC–Co(II) complexes, these spectra are

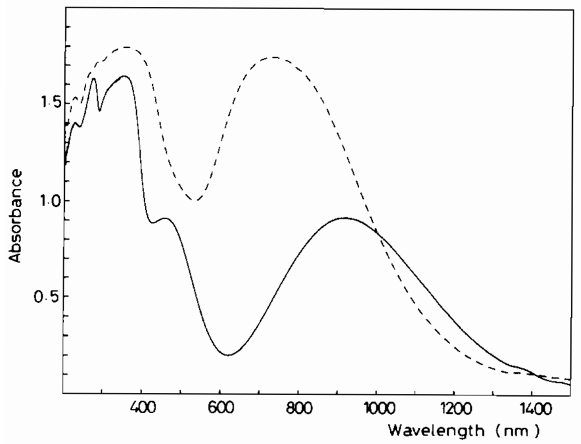

Fig. 2. Diffuse reflectance electronic spectra of $[Co(CNR)_4](ClO_4)_2$ (——) and $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ (– – –), where R = $2,6\text{-}Me_2C_6H_3$.

reasonable for square pyramidal coordination of Co(II) by five strong-field ligands and/or pseudo-octahedral coordination, including a weakly coordinated H_2O [33, 36]. Broad and poorly resolved spectra such as these, however, cannot distinguish between the complex transition patterns expected for the d^7 Co(II) in strong-field square pyramidal or trigonal bipyramidal coordination [36, 37], especially if distortion from idealized geometry takes place in the solid state, which is usually true. Likewise, the spectrum for $[Co(CNR)_4](ClO_4)_2$ does not confirm square planar or distorted square planar coordination, but it is sufficiently similar to known strong-field square planar complexes of Co(II) [14, 38] to support that interpretation.

The structure of $[Co(CNR)_5]ClO_4$ in the solid is interesting in that recrystallization from CH_2Cl_2/ether to form the monosolvated adduct apparently forms a coordination geometry analogous to the type III $[Co(CNC_6H_5)_5]X$, X = ClO_4^-, BF_4^- [7, 28] (C_{2v} – distorted trigonal bipyramid [39]), while recrystallization from $CHCl_3$/ether to form the monochloroform adduct produces the more familiar type II, seen for $[Co(CNR)_5]X$, R = $p\text{-}FC_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$, $p\text{-}IC_6H_4$, $p\text{-}MeC_6H_4$, and $2,6\text{-}Et_2C_6H_3$ [7, 40] (less distorted trigonal bipyramid [41]). The $[Co(CNR)_5]BF_4 \cdot CH_2Cl_2$, however, is a type II structure. Of greater significance, however, is that $[Co(CNR)_5]X$, X = ClO_4^-, BF_4^-, in solution appear to have the same structure, evidenced by a type II $\nu(-N{\equiv}C)$ pattern and similar electronic spectra.

Infrared bands in the region of ν_3, ν_1 for ClO_4^- (1250–850 cm^{-1}) are tabulated in Table 1 and shown in Fig. 3 for the complexes under discussion. The ClO_4^- is clearly undergoing some interaction in most or all of these cases. Whether this interaction is actual coordination to the Co(II), however, is difficult to assess. The number of component bands in ν_3 for

TABLE 1. The $\nu(ClO_4)$ Region for Cobalt Complexes of 2,6-Dimethylphenylisocyanide

Complex[a]	$\nu(ClO_4)$ [b]
$[Co(CNR)_5]ClO_4 \cdot CH_2Cl_2$	1098s, 1085m(sh), 1041w, 974w[c], 921vw[c], 894vw[c], 1155 vw(sh)[c], 1169w[c], 1182w
$[Co(CNR)_5]ClO_4 \cdot CHCl_3$	1097s, 1084s, ~1040w, 974w[c], 922vw[c], 895vw[c], ~1157vw(sh)[c], 1167vw(sh)[c], 1170w, 1181w
$[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$	1098vs, ~1083w(sh), 1121w, 1041s, 1032m(sh), 995vw, 975w[c], 925m[d], 894vw[c]. ~1151vw(sh)[c], 1170w[c], 1180vw, 1208vw[c]
$[Co(CNR)_5](ClO_4)_2 \cdot CH_2Cl_2$	1097vs, ≈1082vw(sh), ≈1120vw(sh), 1038s, ~993vw(sh), 975w[c], 924m[d], ~1154vw(sh)[c], 1171w, 1175vw(sh), ~1208vw[c]
$[Co(CNR)_5](ClO_4)_2 \cdot CHCl_3$	1096vs, ~1082w(sh), ~1118w(sh), 1043s(br), 1021w, 1014vw(sh), ~987vw(sh), 975w(sh)[c], 923m[d], ~915vw(sh), 902w, 1136w, 1172m, 1217vw
$[Co(CNR)_5](ClO_4)_2 \cdot CH_2ClCH_2Cl$	1101vs, 1087m(sh), 1061s(sh), ~1039w(sh), 987vw(sh), 976w[c], 927w[d], 902w, ≈1114vw(sh), ≈1138vw(sh), ~1165vw(sh), 1170vw(sh)[c], 1176w, ~1210vw[c], 1232w
$[Co(CNR)_4](ClO_4)_2 \cdot CH_2Cl_2$	1127vs, ~1114w(sh), 1029s, 1022m(sh), 988w, ~975vw(sh)[c], 915m[d], 905w, 1171m, ~1207vw[c]
$[Co(CNR)_4](ClO_4)_2 \cdot CHCl_3$	1127vs, ~1114w(sh), 1029s, 1021m(sh), 987w, ~977vw(sh)[c], 916m[d], 905w, 1172m, ~1209vw[c]
$[Co(CNR)_4](ClO_4)_2 \cdot CH_2ClCH_2Cl$	1127vs, ~1115w(sh), ~1082vw(sh), 1029s, 1022m(sh), 987w, ~976vw(sh)[c], 936vw(sh), 916m[d], 905w, 1172m, ~1207vw[c]

[a] R = $2,6\text{-}Me_2C_6H_3$. [b] In cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [c] Probably from nujol. [d] Possibly $\nu_1(ClO_4)$.

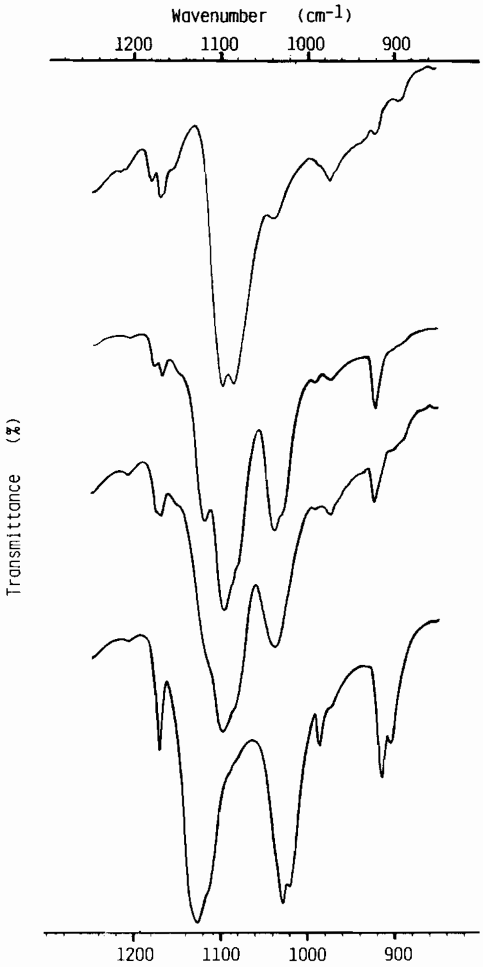

Fig. 3. The $\nu(ClO_4)$ region (nujol/NaCl, 1250–850 cm^{-1}) for $[Co(CNR)_5]ClO_4{\cdot}CHCl_3$, $[Co(CNR)_5]Co(CNR)(ClO_4)_2{\cdot}0.5H_2O$, $[Co(CNR)_5](ClO_4)_2{\cdot}CH_2Cl_2$, and $[Co(NCR)_4](ClO_4)_2{\cdot}CH_2Cl_2$ (top to bottom, respectively), where R = 2,6-$Me_2C_6H_3$.

ClO_4^- is routinely used [42–44] to indicate ClO_4^- coordination: one (ν_3, T_d) for ionic perchlorate, two ($\nu_3 \rightarrow \nu_1 + \nu_4$, C_{3v}) for unidentate coordination, and three ($\nu_3 \rightarrow \nu_1 + \nu_6 + \nu_8$, C_{2v}) for bidentate coordination, although band intensities [44] and degree of component separation [45] are also used to measure coordination. The $[Co(CNR)_4](ClO_4)_2{\cdot}S$, S = CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, complexes have two well-defined, widely-separated bands centered at 1127 and 1029 cm^{-1}, which can be attributed to $\nu_3(ClO_4^-)$. This suggests coordinated perchlorates, $[Co(CNR)_4(ClO_4)_2]$, with both perchlorates acting as unidentate ligands. Weakly-coordinated ClO_4^- in positions axial to a distorted square planar arrangement of the four RNC ligands would be compatible with existing data. These $\nu_3(ClO_4^-)$ patterns and frequencies are in good agreement with other known or postulated examples of perchlorate unidentate coordination, such as $[Ni(CH_3CN)_4(ClO_4)_2]$ (1135s, 1012s cm^{-1}) [46], $[Cu(CH_3CN)_4(ClO_4)_2]$ (1125vs, 1038vs cm^{-1}) [45], $[Cu(H_2O)_2(ClO_4)_2]$ (1158vs, 1030vs cm^{-1}) [45, 47], $[Ni(3\text{-}BrC_5H_4N)_4(ClO_4)_2]$ (1140–1165s, 1025s cm^{-1}) [48], and $[Ni(MeNHCH_2CH_2NH_2)_2(ClO_4)_2]$ (1130vs, 1025vs, cm^{-1}) [49]. The band at 915–916 cm^{-1} could be $\nu_1(ClO_4^-)$ which would become infrared active ν_2 under C_{3v} symmetry. There is slight interference from weak nujol bands, but the complexes decompose under KBr wafer preparation.

Interpretation of $\nu(ClO_4^-)$ for the 'pentakis' complexes is more difficult. All of these complexes might be expected to contain one weakly coordinated unidentate ClO_4^- and one ionic ClO_4^-, as is the case for $[Co(CNPh)_5](ClO_4)_2{\cdot}0.5CH_2ClCH_2Cl$ [34]. This would involve a superposition of the two different $\nu(ClO_4^-)$ patterns, probably leading to incomplete resolution and a rather complex spectrum. Experimental data, as shown for $[Co(CNR)_5](ClO_4)_2{\cdot}CH_2Cl_2$ and $[Co(CNR)_5](ClO_4)_2{\cdot}0.5H_2O$ in Fig. 3, could be thus described. While the apparent pattern is two, albeit asymmetric, bands, the dominant band centered at 1097, 1098 cm^{-1} could be ν_3(ionic), expected at this frequency, overlapping with ν_1(unidentate), expected at somewhat higher frequency (possibly the 1120, 1121 cm^{-1} band resolved in the hydrate, an unresolved shoulder in the dichloromethane adduct). The less-intense, but nevertheless strong, band at 1038, 1041 cm^{-1} would then be ν_4(unidentate). This interpretation seems likely. $[Co(CNR)_5](ClO_4)_2{\cdot}CHCl_3$ is quite similar to $[Co(CNR)_5](ClO_4)_2{\cdot}CH_2Cl_2$, but the spectrum for the corresponding CH_2ClCH_2Cl adduct is very broad and poorly resolved.

The Co(I) complexes, $[Co(CNR)_5]ClO_4{\cdot}CH_2Cl_2$ (type III) and $[Co(CNR)_5]ClO_4{\cdot}CHCl_3$ (type II), would be expected to show ionic perchlorate, since five ligands should satisfy the coordination sphere. Presence of the 1040, 1041 cm^{-1} band, albeit weak, and apparent splitting of the dominant band into two closely-spaced components (1097, 1098; 1084, 1085 cm^{-1}), therefore, is somewhat unexpected. The $[Co(CNPh)_5]ClO_4{\cdot}CHCl_3$ (type I [7, 28], square pyramidal) has ionic perchlorate [50], but these Co(I) complexes (presumably trigonal pyramidal) could be different.

Whereas perchlorate ion coordination is certainly well established, and $Co(CNR)_4(ClO_4)_2$ could almost have been expected to involve some degree of perchlorate interaction, there are two aspects of this example which are interesting. First, there is the relative ease with which the very strongly coordinating ligand RNC is displaced from the coordination sphere. Removing water molecules under reduced pressure and elevated temperature [45, 49] or in the presence of strong dehydrating agents [46, 48] to allow coordination of ionic perchlorate already present in the crystal lattice is easier to understand.

In the enforced absence of strongly coordinating ligands, metal cations will coordinate 'poor' ligands such as ClO_4^-, BF_4^-, PF_6^-, ReO_4^-, AsF_6^-, SbF_6^-, SiF_6^{2-}, BH_4^-, [44] rather than have vacant coordination sites. Here, there seems little explanation for the loss of RNC. Second, there is the pronounced distinction between the perchlorate and tetrafluoroborate salts. While perchlorate is recognized as a stronger ligand than BF_4^- [44], both are weakly coordinating ligands. Possibly the existence of $[Co(CNR)_4]X_2$ is so borderline between dissociation of the $[Co(CNR)_5]X_2$ and reduction to $[Co(CNR)_5]X$ that perchlorate can stabilize this elusive species and BF_4^- cannot. Further investigation is needed for definitive answers.

Solution properties of the three complexes $[Co(CNR)_4](ClO_4)_2$, $[Co(CNR)_5](ClO_4)_2 \cdot 0.5H_2O$ and $[Co(CNR)_5](BF_4)_2 \cdot 0.5H_2O$ are the subjects of continued investigations.

Acknowledgement

We are indebted to the American Society for Engineering Education Summer Faculty Program for partial support of this work in the form of a summer fellowship to C.A.L.B.

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