Synthesis, characterization and molecular structure of tetrakis(2,6-diethylphenylisocyanide)bis(perchlorato)cobalt(II). An example of dissimilarity between perchlorate and tetrafluoroborate salts

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Abstract

Reaction of 2,6-$Et_2C_6H_3NC$ in 5:1 mole ratio with Co(II) produces $Co(CNR)_5X_2 \cdot H_2O$, R = 2,6-$Et_2C_6H_3$; X = ClO_4, BF_4; but the perchlorate salt spontaneously decomposes in solid state to $Co(CNR)_4(ClO_4)_2$. The species $Co(CNR)_4(ClO_4)_2$ was determined by X-ray crystallography to contain equivalent, monodentate, *trans*-coordinated perchlorate ions with average Co–O bond length 2.266(7) Å, and inequivalent arylisocyanide ligands with average Co–C bond lengths 1.896(13) and 1.887(11) Å in approximately square planar coordination (C–Co–C bond angles 87.8(4) and 92.2(4)°, i.e. *trans*-$[Co(CNR)_4(ClO_4)_2]$. Inequivalency of the arylisocyanides is achieved primarily through different tilt of the phenyl rings relative to the CoC_4 plane and location of the perchlorates directly above or below one pair of CNR. The complex crystallizes in triclinic space group $P\bar{1}$ with $a = 11.550(3)$, $b = 13.464(4)$, $c = 15.684(3)$ Å, $\alpha = 77.39(2)$, $\beta = 68.43(2)$, $\gamma = 86.17(3)°$. Final discrepancy values of $R = 0.0726$ ($R_w = 0.0573$) were obtained from 3723 unique, observed reflections. Solid state physical properties (IR, diffuse reflectance and magnetic susceptibility) are compared for $[Co(CNR)_4(ClO_4)_2]$ and $[Co(CNR)_5](BF_4)_2 \cdot H_2O$. Previously reported $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$ should now be formulated as *trans*-$[Co(CNC_6H_3Me_2\text{-}2,6)_4(ClO_4)_2]$, but the tetrafluoroborate ions in both $Co(CNC_6H_3Et_2\text{-}2,6)_5(BF_4)_2 \cdot H_2O$ and $Co(CNC_6H_3Me_2\text{-}2,6)_5(BF_4)_2 \cdot 0.5H_2O$ are probably ionic.

Introduction

Possible ClO_4^- coordination was recognized in $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$, which was prepared from $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2 \cdot 0.5H_2O$, but the analogous $[Co(CNC_6H_3Me_2\text{-}2,6)_4](BF_4)_2$ could not be observed under similar reaction conditions [1]. Assumed $[Co(CNC_6H_3Et_2\text{-}2,6)_5](ClO_4)_2 \cdot xH_2O$ has been used in ligand substitution/reduction reactions to prepare mono- and disubstituted pentakis(arylisocyanide)cobalt(I) complexes, $[Co(CNR)_4L]ClO_4$, L = $P(C_2H_4CN)_3$, $P(NEt_2)_3$ [2]; $[Co(CNR)_3L_2]ClO_4$, L = PPh_3, $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4OMe\text{-}p)_3$, $P(C_6H_{13}\text{-}n)_3$ [2–5]; but it is now recognized that this starting material must have been $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$. This paper describes reaction of 2,6-$Et_2C_6H_3NC$ with both $CoX_2 \cdot 6H_2O$, X = ClO_4, BF_4, and compares the substantially different products.

Perchlorate ion coordination to transition metal cations has been well established by X-ray crystallography since the 1960s [6–8], but is still relatively rare. Usually ClO_4^- coordination takes place when less than six good ligands are available to the coordination sphere. Given the formula $Co(CNR)_4(ClO_4)_2$, perchlorate coordination is not surprising, but starting from $Co(CNR)_5(ClO_4)_2 \cdot H_2O$ it would seem unexpected that ClO_4^- should compete favorably with CNR and spontaneously become a coordinated ion.

Experimental

RNHCHO, R = 2,6-$Et_2C_6H_3$ hereafter, was prepared from commercial RNH_2 (Aldrich) and formic acid [9]. Commercial $Co(ClO_4)_2 \cdot 6H_2O$ and $Co(BF_4)_2 \cdot 6H_2O$ (Strem) were used without recrystallization. Anhydrous diethyl ether was filtered through an alumina column immediately before use.

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Infrared spectra were recorded on a Perkin-Elmer 1710 and Mattson Polaris FT-IR in nujol mull. Electronic spectra were obtained as diffuse reflectance using a Cary model 2390 spectrophotometer. Powdered samples were mounted behind a quartz plate and measured relative to $BaSO_4$. Melting ranges were measured in capillaries using an Electrothermal melting point apparatus. Magnetic susceptibilities were measured at ambient temperature using a JMC (Johnson Matthey Chemicals) magnetic susceptibility balance. Effective magnetic moments were calculated assuming Curie's law behavior; diamagnetic corrections were literature values [10] or were measured. The C, H, N and Cl elemental analyses were obtained from commercial sources; Co was analyzed by atomic absorption using a Baird Alpha 4 AA spectrophotometer. Samples were dissolved in 3 M nitric acid and digested several days before analysis.

Preparation of $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$

RNC was prepared from 2,6-diethylphenylformamide and *p*-toluenesulfonyl chloride in triethylamine by modification [11] of the synthesis by Hertler and Corey [12], and purified by vacuum distillation. 2,6-$Et_2C_6H_3NC$ is a colorless liquid after distillation but rapidly becomes yellow; ν(–N≡C), 2117vs, 2081w cm^{-1} (neat); $X_g = -615 \pm 18 \times 10^{-9}$ (cgs), $X_M = -97.9 \pm 2.9 \times 10^{-6}$. A solution of 6.70 g $Co(BF_4)_2 \cdot 6H_2O$ dissolved in 20.0 ml EtOH was filtered through cotton, chilled in ice, and stirred while 15.67 g RNC (neat, 5:1 mole ratio) was added slowly dropwise. The Co(II) solution became a mixture of viscous green oil and dark blue (azure) crystals; scratching the walls of the reaction flask induced the remaining oil to crystallize. The reaction mixture was filtered cold, separating dark blue microcrystals from yellow–green filtrate. The product was washed with two 5 ml portions of cold EtOH, becoming dark blue when thoroughly dry. Yield: 13.01 g (63%). Melting range: 99–107 °C (decomposition). IR: ν(O–H), 3455m, ~3505w, br(sh) cm^{-1} (nujol); ν(–N≡C), 2201vs, 2155m, 2106w cm^{-1} (nujol). Diffuse reflectance electronic spectrum: ~640br ($A = 1.27$, relative to $BaSO_4$ standard), ~355br (1.30), ~315sh (1.24), 285 (1.22), 255 (1.21), 236 (1.19) nm. $\mu_{eff} = 1.95 \pm 0.02$ BM ($X_g = 958 \pm 28 \times 10^{-9}$). *Anal.* Calc. for $CoC_{55}H_{67}B_2F_8N_5O$: C, 63.11; H, 6.45; N, 6.69; Co, 5.63. Found: C, 63.35; H, 6.47; N, 6.50; Co, 5.3%.

Analogous reaction of RNC (neat, 5:1 mole ratio) with $Co(ClO_4)_2 \cdot 6H_2O$: dark blue (azure) microcrystals; 60% yield; ν(–N≡C), 2198vs, 2153m, 2101w cm^{-1} (nujol). Product was dry and relatively odor-free when initially prepared, but yellow spots were observed shortly after desiccation. Within several days the entire sample became pale yellow. This compound also decomposes stored outside a desiccator, and was not satisfactorily characterized. $[Co(CNR)_5](BF_4)_2 \cdot H_2O$ can be stored indefinitely without apparent decomposition.

TABLE 1. Summary of X-ray diffraction data

Empirical formula	$C_{44}H_{52}N_4O_8Cl_2Co$
Formula weight	894.7
Color, habit	brown prism
Crystal size (mm)	0.12×0.14×0.25
Crystal system	triclinic
Space group	$P\bar{1}$
Cell dimensions	
a (Å)	11.550(3)
b (Å)	13.464(4)
c (Å)	15.684(3)
α (°)	77.39(2)
β (°)	68.43(2)
γ (°)	86.17(3)
Volume ($Å^3$)	2213.3(10)
Z	2
Density (calc.) (Mg/m^3)	1.343
Temperature (K)	223
Diffractometer	Nicolet R3m/V
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Monochromater	highly oriented graphite crystal
Absorption coefficient, μ (mm^{-1})	0.561
2θ Range (°)	3.0–45.0
Scan type	2θ–θ
Scan speed	variable; 7.00 to 15.00°/min in w
Scan range (w)	1.00° plus Kα-separation
Standard reflections	3 measured every 97 reflections
Reflections collected	6380
Independent reflections	5831 ($R_{int} = 1.52\%$)
Observed reflections	3723 ($F > 3.0\sigma(F)$)
R (R_w)	0.0726 (0.0573)
Goodness of fit	1.24
Largest and mean Δ/σ	0.180, −0.001
Difference Fourier excursions ($e/Å^3$)	0.52, −0.60

Recrystallization of $[Co(CNC_6H_3Et_2\text{-}2,6)_4](ClO_4)_2$

A 3.00 g sample of $[Co(CNR)_5](ClO_4)_2 \cdot xH_2O$ was dissolved in 5.5 ml CH_2Cl_2 and filtered through cotton, with 1.0 ml CH_2Cl_2 rinse. Diethyl ether was added dropwise to this initially dark green solution. Formation of crystals was observed after addition of 4.5 ml ether. A total volume of 10.0 ml ether was added and the mixture chilled 30 min before pale orange crystals were filtered from the yellow–brown solution. The crystals were washed with 4.5 ml ether and dried thoroughly before collection. Yield: 1.94 g (83%). Addition of 17.0 ml ether to the filtrate caused precipitation of a second crop of flesh-colored crystals; total yield: 2.10 g (90%). Recrystallization of samples which were mixtures of yellow and blue solid was analogous; all batches produced 85–90% total yield (based on $[Co(CNR)_5](ClO_4)_2 \cdot H_2O$ conversion to [Co(CNR)$_4$](ClO$_4$)$_2$). Melting range: 224–231 °C (decomposition). IR: ν(O–H), absent; ν(–N≡C), 2202vs, 2170w(sh) cm^{-1} (nujol). Electronic spectrum: ~876br (A = 0.994), 461 (0.942), ~349br (1.55), ≈307sh (1.48), ~281sh (1.53), 271 (1.57), ~227 (1.39) nm. μ_{eff} = 1.83 ± 0.02 BM (X_g = 1057 ± 33 × 10^{-9}). *Anal.* Calc. for CoC$_{44}$H$_{52}$Cl$_2$N$_4$O$_8$: C, 59.06; H, 5.86; N, 6.26; Cl, 7.92; Co, 6.59. Found: C, 59.33; H, 5.95; N, 6.21; Cl, 8.00; Co, 6.3%.

X-ray data and structure determination

Pertinent collection parameters are listed in Table 1. The single crystal was mounted on a glass rod and placed in a low temperature N$_2$(g) stream for data collection. The structure was solved by direct methods to locate the Co, C, N, Cl and O atoms. Refinement was by full-matrix least-squares. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2|F_o| + 0.0002(F_o)^2$. Positions and anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogens were included by using a riding model in which the coordinate shifts of the covalently bonded atoms were also applied to the hydrogens (C–H distances held at 0.96 Å), and they were given an overall isotropic parameter of U = 0.06 Å^2. Programs used were part of the Micro VAX II version of the SHELXTL PLUS System [13].

Results and discussion

Molecular structure and atomic numbering scheme for the two inequivalent molecules in the unit cell of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$(ClO$_4$)$_2$] are illustrated in Figs. 1 and 2. Atomic coordinates and equivalent isotropic displacement coefficients are presented in Table 2, with bond lengths and angles listed in Tables 3 and 4, respectively. Comparison of solid-state physical properties for [Co(CNR)$_4$(ClO$_4$)$_2$] and [Co(CNR)$_5$](BF$_4$)$_2$·H$_2$O include ν(–N≡C) in Fig. 3, diffuse reflectance electronic spectra in Fig. 4, and ν(ClO$_4$), ν(BF$_4$) IR in Fig. 5.

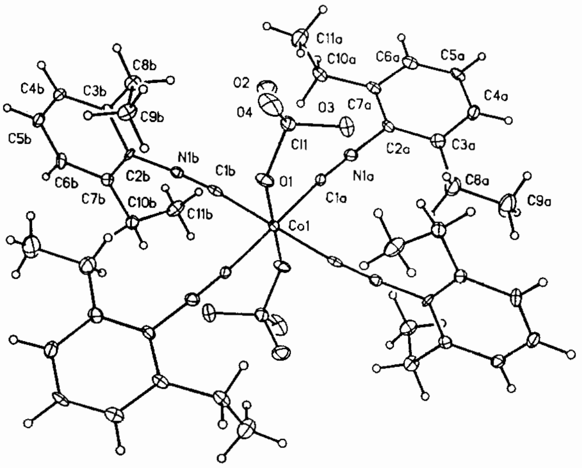

Fig. 1. Thermal ellipsoid plot of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$(ClO$_4$)$_2$] drawn at the 20% probability level, showing one molecule of the two inequivalent molecules per unit cell. Hydrogen atoms omitted for clarity. Perspective in arbitrary orientation.

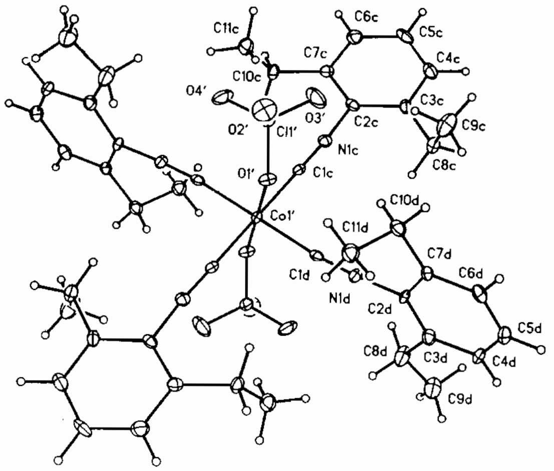

Fig. 2. Thermal ellipsoid plot of [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$(ClO$_4$)$_2$] drawn at the 20% probability level, showing the second molecule of the two inequivalent molecules per unit cell.

X-ray structure results

Two molecules are present in the unit cell (i.e. Z = 2), but there are two crystallographically unique half-molecules in the asymmetric unit, thereby resulting in two distinct (inequivalent) molecules being in the unit cell. Differences between these two molecules are not particularly major, but are sufficient to require consideration of both molecules in all discussions. Thus two sets of data are always presented. Both Co atoms are located on inversion centers, and are co-planar with the four coordinated C atoms, i.e. CoC$_4$ is planar. One pair of equivalent phenyl rings from each molecule, C$_{2a}$–C$_{7a}$ (Fig. 1) (C$_{2c}$–C$_{7c}$ (Fig. 2)), are almost co-planar with CoC$_4$, having dihedral angles of 1.6 (7.8°), while the second equivalent pair of phenyl rings, C$_{2b}$–C$_{7b}$ (C$_{2d}$–C$_{7d}$), are almost perpendicular to the CoC$_4$ plane with dihedral angles of 79.8 (84.5°). Except for monodentate coordination to the Co, the perchlorates appear to be free of strong interaction with other atoms. Shortest non-bonded distances between the oxygens and nearest neighbors, e.g. O–H 2.541, 2.567, 2.672 Å; O–C 3.213, 3.219, 3.232 Å; O–N 3.350 Å; are not seriously shorter than the sum of van der Waals radii [14].

The most significant feature of this structure is coordination of the ClO$_4^-$, which occupy equivalent, *trans* positions. With Co–O bond lengths of 2.259(5)

TABLE 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (Å² × 10³)

	x	y	z	U_{eq}[a]
Co(1)	5000	5000	5000	20(1)
Cl(1)	7580(2)	3617(2)	4524(2)	33(1)
O(1)	6904(5)	4478(4)	4174(3)	36(2)
O(2)	6822(6)	2719(4)	4812(4)	57(3)
O(3)	7805(6)	3816(4)	5299(4)	56(3)
O(4)	8703(6)	3520(5)	3775(4)	68(3)
N(1A)	4732(6)	3674(4)	6895(4)	27(3)
C(1A)	4833(7)	4137(6)	6165(5)	23(3)
C(2A)	4652(7)	3141(6)	7787(5)	26(4)
C(3A)	5106(8)	3630(6)	8292(5)	33(4)
C(4A)	5015(7)	3087(6)	9184(5)	35(4)
C(5A)	4493(8)	2114(6)	9516(5)	35(4)
C(6A)	4042(7)	1662(6)	9007(5)	35(4)
C(7A)	4120(7)	2170(6)	8115(5)	28(4)
C(8A)	5676(9)	4692(6)	7888(6)	55(5)
C(9A)	5943(12)	5227(8)	8532(7)	83(6)
C(10A)	3656(7)	1671(6)	7522(5)	35(4)
C(11A)	4704(9)	1158(7)	6844(7)	59(5)
N(1B)	3816(6)	3517(4)	4331(4)	22(3)
C(1B)	4252(7)	4043(6)	4629(5)	23(3)
C(2B)	3310(8)	2956(5)	3896(5)	21(3)
C(3B)	4077(8)	2224(5)	3459(5)	24(3)
C(4B)	3584(8)	1694(6)	2998(5)	30(4)
C(5B)	2393(8)	1881(6)	3003(5)	31(4)
C(6B)	1657(8)	2596(6)	3442(5)	32(4)
C(7B)	2111(7)	3169(5)	3906(5)	24(3)
C(8B)	5385(7)	2044(6)	3440(5)	33(4)
C(9B)	6318(8)	2850(6)	2739(6)	41(4)
C(10B)	1346(8)	3961(6)	4394(5)	36(4)
C(11B)	854(8)	3651(6)	5459(6)	47(4)
Co(1′)	10000	0	0	23(1)
Cl(1′)	12695(2)	−1191(2)	−877(1)	33(1)
O(1′)	12034(5)	−427(4)	−334(3)	35(2)
O(2′)	13993(5)	−1063(5)	−1088(4)	58(3)
O(3′)	12291(6)	−2167(4)	−342(5)	71(3)
(O4′)	12421(6)	−1014(5)	−1712(4)	59(3)
N(1C)	9175(6)	−2212(5)	429(4)	29(3)
C(1C)	9479(7)	−1366(6)	261(5)	24(3)
C(2C)	8810(7)	−3218(5)	569(5)	28(4)
C(3C)	8775(7)	−3894(6)	1415(5)	32(4)
C(4C)	8426(8)	−4894(6)	1522(6)	43(4)
C(5C)	8165(8)	−5212(6)	827(6)	47(5)
C(6C)	8198(8)	−4517(6)	21(6)	44(4)
C(7C)	8526(7)	−3497(6)	−127(5)	32(4)
C(8C)	9154(8)	−3553(6)	2127(5)	42(4)
C(9C)	10516(9)	−3731(9)	1972(7)	70(6)
C(10C)	8557(8)	−2747(6)	−994(5)	34(4)
C(11C)	9885(8)	−2544(7)	−1733(6)	45(4)
N(1D)	10073(6)	−382(5)	1961(4)	28(3)
C(1D)	9987(5)	−196(5)	1239(6)	25(4)
C(2D)	10302(7)	−655(6)	2805(5)	23(3)
C(3D)	9367(8)	−502(6)	3636(5)	33(4)
C(4D)	9616(8)	−817(6)	4449(5)	36(4)
C(5D)	10745(8)	−1250(6)	4419(6)	40(4)
C(6D)	11646(8)	−1389(6)	3592(6)	36(4)
C(7D)	11448(8)	−1091(5)	2755(5)	28(4)
C(8D)	8142(8)	−36(7)	3616(6)	56(5)
C(9D)	7103(9)	−69(8)	4530(6)	62(5)
C(10D)	12436(7)	−1224(6)	1847(5)	36(4)
C(11D)	13149(8)	−218(6)	1305(6)	42(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å)

Co(1)–O(1)	2.259(5)	Co(1)–C(1A)	1.890(7)
Co(1)–C(1B)	1.895(9)	Co(1)–O(1A)	2.259(5)
Co(1)–C(1AA)	1.890(7)	Co(1)–C(1BA)	1.895(9)
Cl(1)–O(1)	1.474(6)	Cl(1)–O(2)	1.431(6)
Cl(1)–O(3)	1.414(8)	Cl(1)–O(4)	1.416(6)
N(1A)–C(1A)	1.145(10)	N(1A)–C(2A)	1.399(10)
C(2A)–C(3A)	1.385(14)	C(2A)–C(7A)	1.390(10)
C(3A)–C(4A)	1.400(11)	C(3A)–C(8A)	1.517(11)
C(4A)–C(5A)	1.388(11)	C(5A)–C(6A)	1.356(14)
C(6A)–C(7A)	1.390(11)	C(7A)–C(10A)	1.513(13)
C(8A)–C(9A)	1.487(17)	C(10A)–C(11A)	1.529(12)
N(1B)–C(1B)	1.157(12)	N(1B)–C(2B)	1.399(12)
C(2B)–C(3B)	1.399(10)	C(2B)–C(7B)	1.390(12)
C(3B)–C(4B)	1.393(13)	C(3B)–C(8B)	1.504(12)
C(4B)–C(5B)	1.380(13)	C(5B)–C(6B)	1.369(11)
C(6B)–C(7B)	1.406(13)	C(7B)–C(10B)	1.496(11)
C(8B)–C(9B)	1.520(10)	C(10B)–C(11B)	1.522(11)
Co(1′)–O(1′)	2.274(5)	Co(1′)–C(1C)	1.884(8)
Co(1′)–C(1D)	1.898(9)	Co(1′)–O(1′A)	2.274(5)
Co(1′)–C(1CA)	1.884(8)	Co(1′)–C(1DA)	1.898(9)
Cl(1′)–O(1′)	1.472(5)	Cl(1′)–O(2′)	1.425(7)
Cl(1′)–O(3′)	1.402(6)	Cl(1′)–O(4′)	1.424(7)
N(1C)–C(1C)	1.160(10)	N(1C)–C(2C)	1.391(10)
C(2C)–C(3C)	1.425(11)	C(2C)–C(7C)	1.379(14)
C(3C)–C(4C)	1.388(12)	C(3C)–C(8C)	1.503(14)
C(4C)–C(5C)	1.387(16)	C(5C)–C(6C)	1.388(12)
C(6C)–C(7C)	1.396(12)	C(7C)–C(10C)	1.496(11)
C(8C)–C(9C)	1.512(14)	C(10C)–C(11C)	1.542(10)
N(1D)–C(1D)	1.145(12)	N(1D)–C(2D)	1.410(11)
C(2D)–C(3D)	1.400(10)	C(2D)–C(7D)	1.394(12)
C(3D)–C(4D)	1.381(13)	C(3D)–C(8D)	1.517(13)
C(4D)–C(5D)	1.380(13)	C(5D)–C(6D)	1.374(11)
C(6D)–C(7D)	1.384(13)	C(7D)–C(10D)	1.500(10)
C(8D)–C(9D)	1.487(11)	C(10D)–C(11D)	1.538(10)

(2.274(5) Å), this is a shorter Co–O bond than in $[Co(CH_3S(CH_2)_2SCH_3)_2(ClO_4)_2]$ (2.34(2) Å) [6] and significantly shorter than the weak ClO_4^- coordination reported in $[Co(CNC_6H_5)_5ClO_4]ClO_4 \cdot 0.5CH_2ClCH_2Cl$ (2.594(10) Å) [15], but still substantially longer than that expected for a Co–O single bond, as in $[Co(C_3H_6O_3)]_n$ (1.99(6) Å) [16]. (The short bond length of 2.10 Å reported for $[Co(Ph_2MeAsO)_4ClO_4]ClO_4$ [7] was not fully refined.) The Cl–O_1 bond length of 1.474(6) (1.472(5) Å) is slightly lengthened relative to the average 1.420(8) (1.417(8) Å) Cl–O bond length involving non-coordinated oxygen atoms. The 1.420 Å bond length compares well with the average 1.425(20) Å value observed for $HClO_4 \cdot H_2O$ [17]. The averaged O_1–Cl–O angles of 108.3(6) (108.2(6)°) show a slight decrease from perfect tetrahedral 109.5°, while averaged O–Cl–O angles between non-coordinated oxygen atoms of 110.7(7) (110.6(7)°) show a slight increase. These are relatively small distortions for a tetrahedral anion which is reasonably well coordinated through one oxygen atom. The Cl–O_1–Co

TABLE 4. Bond angles (°)

O(1)–Co(1)–C(1A)	97.0(2)	O(1)–Co(1)–C(1B)	89.9(3)
C(1A)–Co(1)–C(1B)	93.5(3)	O(1)–Co(1)–O(1A)	180.0(1)
C(1A)–Co(1)–O(1A)	83.0(2)	C(1B)–Co(1)–O(1A)	90.1(3)
O(1)–Co(1)–C(1AA)	83.0(2)	C(1A)–Co(1)–C(1AA)	180.0(1)
C(1B)–Co(1)–C(1AA)	86.5(3)	O(1A)–Co(1)–C(1AA)	97.0(2)
O(1)–Co(1)–C(1BA)	90.1(3)	C(1A)–Co(1)–C(1BA)	86.5(3)
C(1B)–Co(1)–C(1BA)	180.0(1)	O(1A)–Co(1)–C(1BA)	89.9(3)
C(1AA)–Co(1)–C(1BA)	93.5(3)	O(1)–Cl(1)–O(2)	108.4(4)
O(1)–Cl(1)–O(3)	109.1(4)	O(2)–Cl(1)–O(3)	109.7(4)
O(1)–Cl(1)–O(4)	107.3(3)	O(2)–Cl(1)–O(4)	110.6(4)
O(1)–Cl(1)–O(4)	111.7(4)	Co(1)–O(1)–Cl(1)	125.4(3)
C(1A)–N(1A)–C(2A)	177.2(9)	Co(1)–C(1A)–N(1A)	175.2(8)
N(1A)–C(2A)–C(3A)	116.9(6)	N(1A)–C(2A)–C(7A)	118.9(8)
C(3A)–C(2A)–C(7A)	124.2(7)	C(2A)–C(3A)–C(4A)	116.2(7)
C(2A)–C(3A)–C(8A)	121.2(7)	C(4A)–C(3A)–C(8A)	122.6(9)
C(3A)–C(4A)–C(5A)	120.1(9)	C(4A)–C(5A)–C(6A)	122.2(8)
C(5A)–C(6A)–C(7A)	119.7(7)	C(2A)–C(7A)–C(6A)	117.6(8)
C(2A)–C(7A)–C(10A)	121.6(7)	C(6A)–C(7A)–C(10A)	120.8(7)
C(3A)–C(8A)–C(9A)	117.5(7)	C(7A)–C(10A)–C(11A)	112.0(8)
C(1B)–N(1B)–C(2B)	174.5(6)	Co(1)–C(1B)–N(1B)	174.2(6)
N(1B)–C(2B)–C(3B)	116.4(8)	N(1B)–C(2B)–C(7B)	118.9(7)
C(3B)–C(2B)–C(7B)	124.6(8)	C(2B)–C(3B)–C(4B)	116.2(8)
C(2B)–C(3B)–C(8B)	122.7(8)	C(4B)–C(3B)–C(8B)	121.1(7)
C(3B)–C(4B)–C(5B)	120.6(7)	C(4B)–C(5B)–C(6B)	122.1(9)
C(5B)–C(6B)–C(7B)	120.0(8)	C(2B)–C(7B)–C(6B)	116.5(7)
C(2B)–C(7B)–C(10B)	121.4(8)	C(6B)–C(7B)–C(10B)	122.1(8)
C(3B)–C(8B)–C(9B)	113.7(6)	C(7B)–C(10B)–C(11B)	114.3(6)
O(1′)–Co(1′)–C(1C)	92.8(3)	O(1′)–Co(1′)–C(1D)	83.0(3)
C(1C)–Co(1′)–C(1D)	89.0(3)	O(1′)–Co(1′)–O(1′A)	180.0(1)
C(1C)–Co(1′)–O(1′A)	87.2(3)	C(1D)–Co(1′)–O(1′A)	97.0(3)
O(1′)–Co(1′)–C(1CA)	87.2(3)	C(1C)–Co(1′)–C(1CA)	180.0(1)
C(1D)–Co(1′)–C(1CA)	91.0(3)	O(1′A)–Co(1′)–C(1CA)	92.8(3)
O(1′)–Co(1′)–C(1DA)	97.0(3)	C(1C)–Co(1′)–C(1DA)	91.0(3)
C(1D)–Co(1′)–C(1DA)	180.0(1)	O(1′A)–Co(1′)–C(1DA)	83.0(3)
C(1CA)–Co(1′)–C(1DA)	89.0(3)	O(1′)–Cl(1′)–O(2′)	107.6(4)
O(1′)–Cl(1′)–O(3′)	109.3(3)	O(2′)–Cl(1′)–O(3′)	110.4(4)
O(1′)–Cl(1′)–O(4′)	107.9(4)	O(2′)–Cl(1′)–O(4′)	111.1(4)
O(3′)–Cl(1′)–O(4′)	110.4(5)	Co(1′)–O(1′)–Cl(1′)	126.3(4)
C(1C)–N(1C)–C(2C)	176.1(8)	Co(1′)–C(1C)–N(1C)	178.8(8)
N(1C)–C(2C)–C(3C)	117.9(8)	N(1C)–C(2C)–C(7C)	117.8(7)
C(3C)–C(2C)–C(7C)	124.3(7)	C(2C)–C(3C)–C(4C)	116.2(9)
C(2C)–C(3C)–C(8C)	121.7(7)	C(4C)–C(3C)–C(8C)	122.1(7)
C(3C)–C(4C)–C(5C)	121.3(8)	C(4C)–C(5C)–C(6C)	120.1(8)
C(5C)–C(6C)–C(7C)	121.6(10)	C(2C)–C(7C)–C(6C)	116.5(7)
C(2C)–C(7C)–C(10C)	121.9(7)	C(6C)–C(7C)–C(10C)	121.6(9)
C(3C)–C(8C)–C(9C)	112.6(7)	C(7C)–C(10C)–C(11C)	112.8(7)
C(1D)–N(1D)–C(2D)	174.0(7)	Co(1′)–C(1D)–N(1D)	173.1(6)
N(1D)–C(2D)–C(3D)	118.7(7)	N(1D)–C(2D)–C(7D)	117.0(6)
C(3D)–C(2D)–C(7D)	124.2(8)	C(2D)–C(3D)–C(4D)	116.6(8)
C(2D)–C(3D)–C(8D)	120.1(8)	C(4D)–C(3D)–C(8D)	123.3(7)
C(3D)–C(4D)–C(5D)	120.4(7)	C(4D)–C(5D)–C(6D)	121.7(9)
C(5D)–C(6D)–C(7D)	120.6(8)	C(2D)–C(7D)–C(6D)	116.5(7)
C(2D)–C(7D)–C(10D)	122.6(8)	C(6D)–C(7D)–C(10D)	120.9(8)
C(3D)–C(8D)–C(9D)	117.6(8)	C(7D)–C(10D)–C(11D)	111.0(6)

angle of 125.4(3) (126.3(4)°) is smaller than that observed for other coordinated ClO_4^-, 130° [7], 135.6(7)° [15], but longer than those for common oxygen covalent bonds, such as 104.5° (H–O–H) [14], 110.0° (Me–O–Me) [14], 123(1)° ($O_3Cr–O–CrO_3^{2-}$, in $Rb_2Cr_2O_7$) [18]. The two ClO_4^- are in equivalent, *trans* positions, i.e. O_1–Co–O_{1A} is perfectly linear, 180.0(1) (180.0(1)°), but the O_1–Co–O_{1A} axis is tilted 7.0(2) (7.2(3)°) from normal to the CoC_4 plane, thereby placing one ClO_4^- nearer to each equivalent

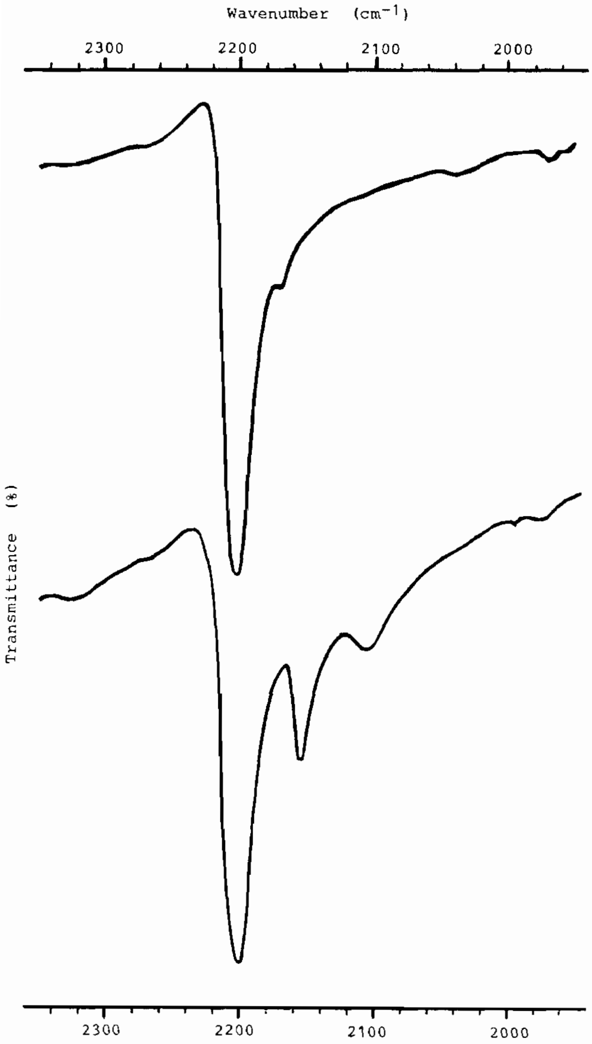

Fig. 3. The ν(–N≡C) pattern for [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$(ClO$_4$)$_2$] (top) and [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$](BF$_4$)$_2$·H$_2$O (bottom).

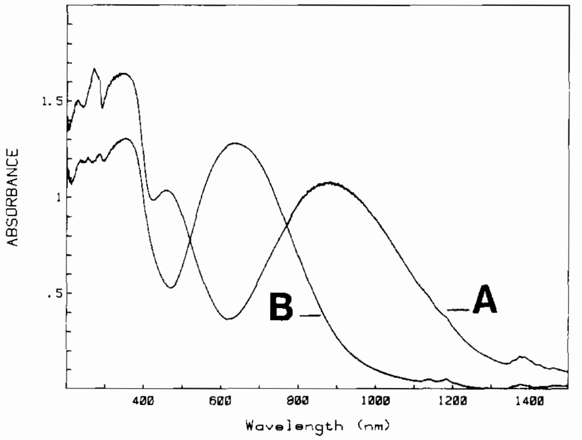

Fig. 4. Diffuse reflectance electronic spectra for [Co(CNC$_6$H$_3$Et$_2$-2,6)$_4$(ClO$_4$)$_2$] (A) and [Co(CNC$_6$H$_3$Et$_2$-2,6)$_5$](BF$_4$)$_2$·H$_2$O (B).

CNR with the shorter Co–C bond. This positioning over/under two CNR accentuates their inequivalency with the other two CNR.

Arylisocyanide coordination to Co(II) is only approximately square planar. Whereas the Co–C bond lengths are almost identical, 1.895(9) and 1.890(7) Å (1.898(9), 1.884(8) Å), and CoC$_4$ is planar, the two different C–Co–C bond angles are unequal; 86.5(3) and 93.5(3)° (89.0(3), 91.0(3)°). This rectangular planar coordination combined with positioning of the ClO$_4^-$ and tilt of the phenyl rings, leads to inequivalent pairs of CNR ligands, reflected in the doubled ν(–N≡C). Many Co(CNR)$_4^{2+}$ units experimentally show inequivalent CNR, but possibly through different distortions. The CNR in [Co(CNC$_6$H$_4$Me-*p*)$_4$I$_2$], for example, are inequivalent pairs with equal Co–C bond lengths because of 5° S$_4$/C$_2$ puckering of the CoC$_4$ equatorial plane [19]. The averaged Co–C bond lengths of 1.896(9) and 1.887(9) Å compare satisfactorily with 1.81(4) Å in [Co(CNC$_6$H$_4$Me-*p*)$_4$I$_2$] [19], 1.84(2) Å average basal Co–C in [Co(CNC$_6$H$_5$)$_5$ClO$_4$]ClO$_4$·0.5CH$_2$ClCH$_2$Cl [15], and 1.82–1.92 Å in [Co$_2$(CNCH$_3$)$_{10}$](ClO$_4$)$_4$ [20]. This Co(II)–C bond length is also quite similar to bond lengths observed for Co(III)–C, as 1.89 Å in K$_3$[Co(CN)$_5$CF$_2$CHF$_2$] [21]; and Co(I)–C, as 1.88(3), 1.84(2), 1.83(2) Å in [Co(CNC$_6$H$_5$)$_5$]ClO$_4$·HCCl$_3$ [22]; 1.85(1), 1.83(2) Å in [Co(CNC$_6$H$_4$F-*p*)$_3${P(OCH$_3$)$_3$}$_2$]BF$_4$ [23]; and 1.88(2), 1.88(2), 1.84(2) Å in [Co(CNCH$_3$)$_5$]ClO$_4$ [24]. The oxidation state of Co therefore seems to have little effect on the Co–C bond length, and since all these bond distances are significantly shorter than the value proposed for a Co–C single bond, 2.15 Å [20], multiple bond character is usually invoked [15, 19–24]. Substantial d$_\pi$–π^* backbonding has always been maintained for organoisocyanide complexes of transition metals.

The average C≡N bond length of 1.152(12) (1.152(12) Å) and N–C bond length of 1.399(12) (1.400(12) Å) are in good agreement with other Co(II)–arylisocyanide structures, 1.14(4) [19], 1.16 (fixed) [15]; 1.38(5) [19], 1.368(11)) [15] Å; and with free arylisocyanide molecules, average 1.16 Å [25]; or standard N–C bonds, 1.38 Å [14]. The observed Co–C–N bond angles, 175.2(8), 174.2(6) (178.8(8), 173.1(6)°), and C–N–C angles, 177.2(9), 174.5(6) (176.1(8), 174.0(7)°), show comparable or less deviation from perfect linearity compared to other Co(II)–organoisocyanide structures. Angles decreased to 172.8(12) and 173.5(10)° were reported for [Co(CNC$_6$H$_5$)$_5$ClO$_4$]ClO$_4$·0.5CH$_2$ClCH$_2$Cl [15], 169.3(2.9) and 170.7(4.0)° for [Co$_2$(CNCH$_3$)$_{10}$](ClO$_4$)$_4$ [20], and 178.8(42) and 174.4(44)° for [Co(CNC$_6$H$_4$Me-*p*)$_4$I$_2$] [19]. Bond lengths and angles in the hydrocarbon portions of the CNR ligands also show reasonably small deviations from idealized ge-

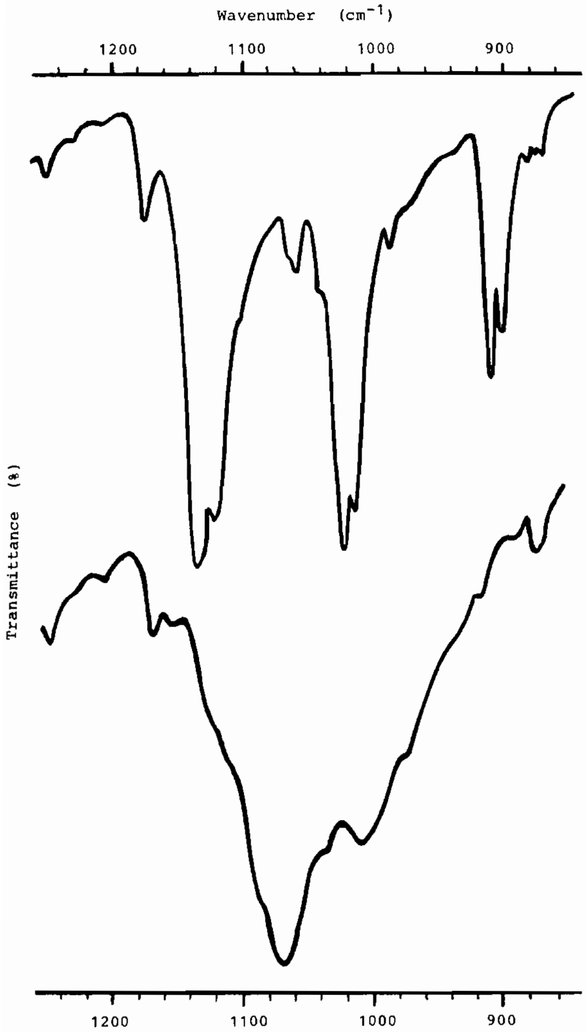

Fig. 5. The IR 1250–850 cm^{-1} (nujol/NaCl) for $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ (top) and $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ (bottom).

ometry. The overall molecular structure for $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$, then, is free from major distortions, especially the almost-tetrahedral ClO_4^-.

[Co(CNR)$_4$(ClO$_4$)$_2$]

Similarity between $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ and previously reported $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$ [1] is very strong. In addition to identical color and solubility behavior, measured physical properties for these two complexes are very similar. The $\nu(\text{–N}\equiv\text{C})$ (see Fig. 2 and Fig. 1, ref. 1) are identical in pattern, the 2 cm^{-1} frequency difference being seen also in the free RNC [26]. Effective magnetic moments of 1.83 ± 0.02 BM for $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ and 1.84 ± 0.02 BM for $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$ (re-measured) both indicate one-electron paramagnetism. Diffuse reflectance electronic spectra (Fig. 3 and Fig. 2, ref. 1) are also similar in overall appearance of number and relative intensities for resolved bands. Only the very broad, lowest-energy (first crystal field) band shows significant difference in wavelengths; ~876 nm in $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ and ~919 nm in $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$. The $\nu(ClO_4)$ IR for these complexes (Fig. 4 and Fig. 3, ref. 1) are also very similar. In $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ the pattern is complicated by the presence of a 1059w band (from RNC) between ν_1, ν_4 [27, 28] at 1135 and 1022 cm^{-1} (1127 and 1029 cm^{-1} in $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$ [1]), but ν_1, ν_4 (the unsplit ν_3 for anionic, symmetrical ClO_4^- [27, 28]) are clearly the dominant features in both spectra. The 910s cm^{-1} band (915–916 cm^{-1} in $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$ [1]) should be the ν_2 for monodentate ClO_4^- (the IR-inactive ν_1 for ionic (T_d) ClO_4^- which becomes IR-active ν_2 under C_{3v} symmetry of monocoordinated ClO_4^-).

Physical measurements suggest structural analogy between $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ and $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$, which is now probably better formulated as *trans*-$[Co(CNC_6H_3Me_2\text{-}2,6)_4(ClO_4)_2]$, with two monodentate ClO_4^-. This is what we previously predicted [1] on the basis of $\nu(ClO_4)$.

[Co(CNR)$_5$]X$_2$·xH$_2$O

Similarity between $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ and $[Co(CNC_6H_3Me_2\text{-}2,6)_5](BF_4)_2 \cdot 0.5H_2O$ is not as pronounced as between the tetrakis complexes. The $\nu(\text{–N}\equiv\text{C})$ for both $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X_2 \cdot xH_2O$, $X = ClO_4$, BF_4, are different from all other pentakis(arylisocyanide)cobalt(II) complexes observed [26]. The strongest band at 2198, 2201vs cm^{-1} is expected, but 2153, 2155m and 2101, 2106w cm^{-1} are low enough to suggest Co(I). Since the $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ could be washed with cold EtOH and recrystallized from CH_2Cl_2/ether without substantially altering $\nu(\text{–N}\equiv\text{C})$, all three bands are assigned to $[Co(CNR)_5](BF_4)_2 \cdot H_2O$. The electronic spectrum for $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ (Fig. 4) is reasonably similar to those of $[Co(CNC_6H_3Me_2\text{-}2,6)_5]X_2 \cdot 0.5H_2O$, $X = BF_4$, ClO_4 [1], except for substantial displacement of the broad, lowest-energy band to 640 nm, from 745 and 733 nm, respectively. Effective magnetic moment of 1.95 BM indicates one-electron paramagnetism.

The $\nu(BF_4)$ IR for $[Co(CNC_6H_3Me_2\text{-}2,6)_5](BF_4)_2 \cdot 0.5H_2O$ was not previously discussed [1], but comparison with $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ (Fig. 5) shows them to be similar. Spectra for $[Co(CNC_6H_3Me_2\text{-}2,6)_5](BF_4)_2 \cdot Y$ ($Y = 0.5H_2O$, CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl) and $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ in nujol are all best interpreted as one intense broad band, with numerous shoulders. This is unlike $\nu(ClO_4)$ for derivatives of $[Co(CNC_6H_3Me_2\text{-}2,6)_4](ClO_4)_2$ (see Fig. 3, ref. 1), which are best interpreted as two, albeit unequal, bands. Whereas $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2$ could be explained as having one ionic and one unidentate ClO_4^- [1], both BF_4^- in both $[Co(CNC_6H_3Me_2\text{-}2,6)_5](BF_4)_2 \cdot 0.5H_2O$ and $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ are probably strictly ionic.

$[Co(CNC_6H_3Et_2\text{-}2,6)_5](ClO_4)_2 \cdot xH_2O$ was only partially characterized, but is probably analogous to both $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$ and $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2 \cdot 0.5H_2O$. Azure crystals, which decomposed before characterization was complete, were obtained on two occasions; thereafter on subsequent attempts the product failed to crystallize promptly and only $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$ was eventually isolated. $[Co(CNC_6H_3Et_2\text{-}2,6)_5](ClO_4)_2 \cdot xH_2O$ does exist, but is significantly less stable than $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2 \cdot 0.5H_2O$ or $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$, which appear to be stable indefinitely at room conditions. Ease of $[Co(CNR)_4(ClO_4)_2]$ preparation therefore appears to be $R = 2,6\text{-}Et_2C_6H_3 > 2,6\text{-}Me_2C_6H_3$, which could suggest that increased steric hindrance in the arylisocyanide facilitates ClO_4^- coordination. This possibility is currently being investigated.

Supplementary material

The first author may be contacted for supplementary tables of anisotropic thermal parameters for the non-hydrogen atoms, calculated hydrogen atom positions and their isotropic displacement coefficients, and observed and calculated structure factors of $[Co(CNC_6H_3Et_2\text{-}2,6)_4(ClO_4)_2]$.

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