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### Addition Complexes of *Tetrais(t-Butylisocyanide)Cobalt(II) Perchlorate* with Nitrogen Bases

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# ADDITION COMPLEXES OF *TETRAKIS(t-BUTYLISOCYANIDE)COBALT(II)* PERCHLORATE WITH NITROGEN BASES

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Reaction of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  with selected aromatic and cyclic aliphatic amines and thioureas, either by dissolution or digestion, leads to complexes of the form  $[\text{Co}(\text{CNCMe}_3)_4\text{L}_2](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ;  $\text{L} = \text{C}_5\text{H}_5\text{N}$ , 3-MeC<sub>5</sub>H<sub>4</sub>N, 4-MeC<sub>5</sub>H<sub>4</sub>N, C<sub>9</sub>H<sub>7</sub>N, C<sub>5</sub>H<sub>10</sub>NH, 3-MeC<sub>5</sub>H<sub>9</sub>NH, 4-MeC<sub>5</sub>H<sub>9</sub>NH, HN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, H<sub>2</sub>NC(S)NH<sub>2</sub>, EtHNC(S)NH<sub>2</sub>. Steric hindrance decreases reactivity of the amine and stability of the complex. Characterization by IR, diffuse reflectance electronic spectra, and magnetic susceptibility suggests tetragonal coordination.

**Keywords:** Alkylisocyanide, cobalt(II) complexes, addition complexes, nitrogen bases.

## INTRODUCTION

Coordination of five organoisocyanide ligands with cobalt(II) perchlorate is well-established for both alkylisocyanides<sup>1–4</sup> and arylisocyanides,<sup>1,5–9</sup> so synthesis of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$ <sup>10</sup> was unexpected. Colour changes between solid and solution suggest that a different coordination mode occurs when the complex is dissolved in Lewis bases. This present work investigates reactions between  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  and nitrogen bases; complexes of the form  $[\text{Co}(\text{CNCMe}_3)_4\text{L}_2](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$  are prepared.

Reaction of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  with aromatic amines is significantly different to the behaviour of arylisocyanide-Co(II) complexes. Treatment of  $[\text{Co}(\text{CNR})_5](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$  (R = aryl) with pyridine produces  $[\text{Co}(\text{CNR})_5]\text{ClO}_4$  in good yield.<sup>11,12</sup>

## EXPERIMENTAL

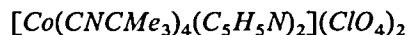
### *Reagents*

$[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  was prepared from commercial CNCMe<sub>3</sub> (Fluka) as previously reported.<sup>10</sup> Commercial amines (Fluka) were distilled from KOH and stored over molecular sieves (4A): pyridine (C<sub>5</sub>H<sub>5</sub>N), α-picoline (2-MeC<sub>5</sub>H<sub>4</sub>N), β-picoline (3-MeC<sub>5</sub>H<sub>4</sub>N), γ-picoline (4-MeC<sub>5</sub>H<sub>4</sub>N), 2,6-lutidine (2,6-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N) sym-collidine (2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N), quinoline (C<sub>9</sub>H<sub>7</sub>N), quinaldine (2-MeC<sub>9</sub>H<sub>6</sub>N), 2-benzylpyridine (2-C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N), piperidine (C<sub>5</sub>H<sub>10</sub>NH), 2-methylpiperidine (2-MeC<sub>5</sub>H<sub>9</sub>NH), 3-methylpiperidine (3-MeC<sub>5</sub>H<sub>9</sub>NH), 4-methylpiperidine (4-MeC<sub>5</sub>H<sub>9</sub>NH), *N*-methylpiperidine (C<sub>5</sub>H<sub>10</sub>NMe), *N*-ethylpiperidine (C<sub>5</sub>H<sub>10</sub>NEt), piperazine (HN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe), morpholine (HN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O), and pyrrolidine (C<sub>4</sub>H<sub>8</sub>NH). Thiourea (H<sub>2</sub>NC(S)NH<sub>2</sub>), *N,N'*-diethylthiourea (EtHNC(S)NH<sub>2</sub>) and *N,N'*-diphenylthiourea (PhHNC(S)NHPh) were used without further purification. Diethyl ether was filtered through alumina immediately before use.

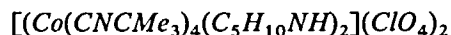
### Instrumentation

IR spectra were recorded on a Mattson Polaris FT-IR instrument. Diffuse reflectance electronic spectra were measured with an integrating sphere on a Shimadzu UV-365 over 860–240 nm. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey magnetic susceptibility balance. Effective magnetic moments were calculated assuming Curie Law behaviour. The Cl and some C, H, and N analyses were performed commercially; other C, H, and N analyses were obtained using a Carlo Erba CHN-O/S 1106 elemental analyzer. Microsamples were weighed on a Sartorius Ultramicro Electrobalance and sealed in tin capsules.

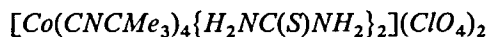
Typical preparations are given below.



A 300 mg sample of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  was dissolved in 8.0 cm<sup>3</sup> of pyridine and filtered through cotton. Then, 10.0 cm<sup>3</sup> of ether was added dropwise while the solution was stirred. The reaction was chilled for 15 min in ice, then the blue microcrystals which had formed were filtered from a yellow solution. Yield: 305 mg (83%). The complex can be recrystallized from C<sub>5</sub>H<sub>5</sub>N/ether and is air-stable.



A 300 mg sample of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  was added to 5.0 cm<sup>3</sup> of freshly-distilled piperidine, and the resulting slurry stirred for 15 min at room temperature. The solid changed from a beige to a blue colour. Sky blue microcrystals were filtered from the pale blue solution, washed twice with 3.0 cm<sup>3</sup> portions of ether, and sucked dry in air. Yield: 340 mg (90%). This compound decomposed in 6–8 days with desiccation.



A 1.00 g sample of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  was slowly added to a solution of 1.56 g of H<sub>2</sub>NC(S)NH<sub>2</sub> (1:12.5 mole ratio) in 75 cm<sup>3</sup> ethanol, and stirred for 5 min at 25°C. The beige solid rapidly produced a green suspension. Dark green microcrystals were filtered from a greenish-yellow solution, washed with 5.0 cm<sup>3</sup> of ethanol, and sucked dry in air. Yield: 1.01 g (83%). This compound is air-stable.

## RESULTS AND DISCUSSION

Diamagnetic susceptibilities for the ligands are tabulated in Table I. Physical properties for the new complexes in the solid-state are summarized in Table II; the complexes decompose in solution. The compounds do not have well-defined melting/decomposition ranges.

### Syntheses of the complexes

Different reaction conditions are necessitated by differing solubilities of  $[\text{Co}(\text{CNCMe}_3)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$  in the various amines. Solubility is relatively high in C<sub>5</sub>H<sub>5</sub>N and C<sub>9</sub>H<sub>7</sub>N, so that the starting material is dissolved and filtered through

TABLE I  
Measured diamagnetic susceptibilities (cgs units).

Ligand	$\chi_g \times 10^9$	$\chi_M \times 10^6$
CNCMe <sub>3</sub>	-647 ± 11	-53.8 ± 0.9
C <sub>3</sub> H <sub>5</sub> N	-560 ± 7	-44.3 ± 0.6
3-MeC <sub>5</sub> H <sub>4</sub> N	-581 ± 6	-54.1 ± 0.6
4-MeC <sub>5</sub> H <sub>4</sub> N	-607 ± 8.5	-56.5 ± 0.8
C <sub>9</sub> H <sub>7</sub> N	-594 ± 9	-76.7 ± 1.2
C <sub>5</sub> H <sub>10</sub> NH	-661 ± 17	-56.3 ± 1.4
3-MeC <sub>5</sub> H <sub>9</sub> NH	-687 ± 11	-68.1 ± 1.1
4-MeC <sub>5</sub> H <sub>9</sub> NH	-676 ± 11	-67.0 ± 1.0
HN(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	-579 ± 12	-50.5 ± 1.0
H <sub>2</sub> NC(S)NH <sub>2</sub>	-521 ± 8	-39.7 ± 0.6
EtHNC(S)NHEt	-591 ± 12	-78.1 ± 1.6

cotton; the complex is precipitated by addition of ether. Solubility is limited in other amines so that the starting material is simply digested in the amine, and ether used for washing and drying. Reaction of thioureas requires an inert solvent. Initial reactions were performed under anhydrous conditions, before observation indicated that the reactions are not air or moisture sensitive.

Limited stability prevents characterization of complexes with 2-MeC<sub>5</sub>H<sub>4</sub>N, 2-MeC<sub>5</sub>H<sub>9</sub>NH, HN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe, and C<sub>4</sub>H<sub>8</sub>NH. Complexes of the form [Co(CNCMe<sub>3</sub>)<sub>4</sub>L<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, are believed to be initially prepared, but satisfactory elemental analyses could not be obtained. Compositions indicate partial loss of amine. The complexes with aliphatic amines in general, especially 3-MeC<sub>5</sub>H<sub>9</sub>NH and 4-MeC<sub>5</sub>H<sub>9</sub>NH, tend to have limited stability and decompose within days whether desiccated or exposed to the atmosphere. Instability of complexes with 2-MeC<sub>5</sub>H<sub>4</sub>N and possibly 2-MeC<sub>5</sub>H<sub>9</sub>NH is probably due to steric hindrance of the amine. Severe steric hindrance in the amine appears to prevent complex formation altogether. No reaction was observed with 2,6-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, 2,4,6-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N, 2-MeC<sub>9</sub>H<sub>6</sub>N, 2-C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N, C<sub>5</sub>H<sub>10</sub>NMe or C<sub>5</sub>H<sub>10</sub>NEt; unreacted starting material was recovered in good yield. Decomposition of [Co(CNCMe<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> was observed on attempted reaction with PhHNC(S)NHPh.

#### Characterization of the complexes

Nujol-mull IR spectra, diffuse reflectance electronic spectra and magnetic susceptibilities have been measured (see Table II). Physical measurements are compatible with tetragonal coordination, *i.e.*, *trans*-[Co(CNCMe<sub>3</sub>)<sub>4</sub>L<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O. The H<sub>2</sub>O molecule, which may or may not be present depending on the N-ligand and method of preparation, is probably not coordinated (unsplit  $\nu(\text{O}-\text{H})$  patterns). The  $\nu(-\text{N}\equiv\text{C})$  pattern of one strong band with a lower-energy, unresolved shoulder is characteristic for a distorted tetragonal arrangement of four organoisonocyanide ligands, as in *trans*-[Co(CNR)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>], R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,<sup>13</sup> 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.<sup>14</sup> Regular arrangement of the four RNC ligands (*D*<sub>4h</sub>) should give rise to a single  $\nu(-\text{N}\equiv\text{C})$  mode. The weak band at 2020–2035 cm<sup>-1</sup>, seen also in the free ligand and starting material, is probably non-fundamental.

TABLE II  
Physical properties for addition complexes of tetrakis(*t*-butylisocyanide)cobalt(II) perchlorate.

Compound/colour	IR spectra <sup>a</sup>	Electronic spectra <sup>b</sup>		Magnetic suscept. $\chi_g \times 10^6/\mu_{\text{eff}}$	Elemental analysis				found/calc
	$\nu(-N\equiv C)$	spectra <sup>b</sup>			C	H	N	Cl	
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> (C <sub>3</sub> H <sub>7</sub> N) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> Pale blue	2210 vs ~2176 w(sh) 2021 w	632br (0.54) 324 (1.10) ~264sh (1.10) ~248sh (1.11)		1.50 ± 0.03 1.90 ± 0.02 BM	39.48 39.21	6.30 6.30	9.21 9.18	11.65 11.94	
Co(CNCMe <sub>3</sub> ) <sub>4</sub> (4-MeC <sub>3</sub> H <sub>4</sub> N) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Medium blue	~2212 w(sh) 2204 vs ~2176 vw(sh) ~2168 vw(sh) 2026 w	638br (0.60) 324 (1.10) 252 (1.13)		1.85 ± 0.04 2.09 ± 0.02 BM	48.46 48.37	6.47 6.34	10.84 10.58	8.95 9.06	
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> (3-MeC <sub>3</sub> H <sub>4</sub> N) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Pale blue	2213 vs 2178 w(sh) 2025 w	634br (0.50) ~390sh 324 (1.06) 254 (1.21)		2.74 ± 0.04 2.49 ± 0.02 BM	48.95 48.37	6.52 6.34	10.55 10.58	8.80 9.06	
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> (C <sub>3</sub> H <sub>7</sub> N) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Pale green	2213 vs ~2180 w(sh) 2025 w	636br (0.50) ~400sh ~308sh (1.17) ~260br (1.15)		1.84 ± 0.04 2.22 ± 0.02 BM	52.66 52.66	6.05 6.14	9.70 9.64	8.48 8.74	
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> (C <sub>3</sub> H <sub>10</sub> NH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> Pale sky blue	2210 vs ~2176 w(sh) 2032 w	636br (0.43) 355 (0.88) 294 (1.10) 258 (1.21)		2.72 ± 0.02 2.43 ± 0.01 BM	47.43 47.37	7.90 7.69	10.93 11.05	9.09 9.32	

[Co(CNCMe <sub>3</sub> ) <sub>4</sub> (4-MeC <sub>3</sub> H <sub>9</sub> NH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Pale sky blue	~2236 w(sh)	~670sh (0.49) <sup>f</sup>	1.53 ± 0.03	47.13	7.83	10.46	8.65
	≈2217 w(sh) 2205 vs ~2171 w(sh) 2029 w	~636sh (0.49) <sup>f</sup> 358 (0.93) ~290sh (1.12) 258 (1.21)	2.00 ± 0.01 BM	47.64	8.00	10.42	8.79
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> (3-MeC <sub>3</sub> H <sub>9</sub> NH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Pale sky blue	2206 vs	~670sh (0.48) <sup>f</sup>	1.63 ± 0.07	46.94	7.82	10.56	8.86
	≈2173 vw(sh) ~2133 vw 2029 w	~620sh (0.48) <sup>f</sup> 361 (1.03) ≈300sh (1.20) 256 (1.23)	2.05 ± 0.03 BM	47.64	8.00	10.42	8.79
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> {HN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> }(ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O Pale sky blue	2212 vs	648sh (0.45)	1.79 ± 0.02	43.14	7.01	10.88	8.95
	2176 w(sh) 2029 w	349 (0.90) 302 (1.10) 258 (1.20)	2.07 ± 0.01 BM	42.97	7.21	10.74	9.06
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> {H <sub>2</sub> NC(S)NH <sub>2</sub> } <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> Dark green	2202 vs	~650sh (0.88) <sup>f</sup>	1.92 ± 0.02	35.05	5.93	14.88	9.41
	~2166 w(sh) 2037 w	~610sh (0.88) <sup>f</sup> 390 (1.17) 355 (1.16) 315 (1.21) ~260sh (1.18)	2.07 ± 0.01 BM	35.58	5.97	15.09	9.55
[Co(CNCMe <sub>3</sub> ) <sub>4</sub> {EtHNC(S)NHEt} <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> Dark yellow-green	~2220 vw(sh)	~700sh (0.89) <sup>f</sup>	1.40 ± 0.02	41.73	7.12	12.94	8.17
	2194 vs ~2157 vw(sh) 2032 w	~630sh (0.89) <sup>f</sup> ≈444sh (1.06) 396 (1.18) ~354sh (1.19) 329 (1.23) ~262 (1.18)	1.99 ± 0.01 BM	42.15	7.07	13.11	8.29

<sup>a</sup>The ν(-N≡C) mode is given in cm<sup>-1</sup>; s=strong, w=weak, v=very, sh=shoulder, br=broad. <sup>b</sup>The λ<sub>max</sub>(ε) values are given in nm and (M<sup>-1</sup>cm<sup>-1</sup>).  
<sup>c</sup>Multiple first band, λ<sub>max</sub> and ε estimated without Gaussian resolution.

Effective magnetic moments, 1.90–2.50 BM, are within the range observed for low-spin Co(II) complexes, 2.0–2.7 BM.<sup>15</sup> This is compatible with tetragonal coordination by strong field ligands. The diffuse reflectance electronic spectra are also compatible with a tetragonal structure. Spectra differ primarily in whether the first band is simply very broad or is partially resolved into two or three bands. Physical properties suggest, but do not confirm, tetragonal coordination.

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