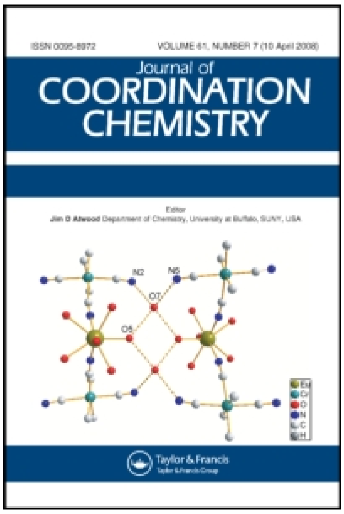

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

REACTIONS OF ISOPROPYLISOCYANIDE AND t-BUTYLISOCYANIDE WITH COBALT(II) PERCHLORATE AND TETRAFLUOROBORATE

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To cite this Article Becker, Clifford A. L.(1993) 'REACTIONS OF ISOPROPYLISOCYANIDE AND t-BUTYLISOCYANIDE WITH COBALT(II) PERCHLORATE AND TETRAFLUOROBORATE', Journal of Coordination Chemistry, 28: 2, 147 — 153

To link to this Article: DOI: 10.1080/00958979308035154

URL: http://dx.doi.org/10.1080/00958979308035154

J. Coord. Chem., 1993, Vol. 28, pp. 147-153
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REACTIONS OF ISOPROPYLISOCYANIDE AND *t*-BUTYLISOCYANIDE WITH COBALT(II) PERCHLORATE AND TETRAFLUOROBORATE

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(*Received June 2, 1992*)

Reaction of isopropylisocyanide with $CoX_2 \cdot 6H_2O$ ($X = ClO_4$, BF_4) in EtOH produced $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$, and reaction of *t*-butylisocyanide, produced $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$. The complexes were characterized by IR, electronic spectra, magnetic susceptibility, and molar conductivity. $CNCHMe_2$ complexes are diamagnetic in the solid state and one-electron paramagnetic in solution; this and other data are consistent with dimerization in the solid and dissociation in solution. $CNCMe_3$ complexes are one-electron paramagnetic in the solid and solution states, this being consistent with a monomeric structure.

Keywords: Isopropylisocyanide, *t*-butylisocyanide, cobalt(II), dinuclear complexes

INTRODUCTION

Organoisocyanide reactions with cobalt(II) have been investigated with arylisocyanides and alkylisocyanides. *Pentakis*(arylisocyanide)cobalt(II) complexes, $[Co(CNR)_5]X_2 \cdot nH_2O$ ($X = ClO_4$, BF_4), are reported for reaction of stoichiometric or excess RNC with Co(II).[1-6] Monomeric *pentakis*(methylisocyanide)cobalt(II) perchlorate, as blue, paramagnetic crystals, was initially reported[1,3,7] for reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with excess CNMe in EtOH, but could not be reproduced.[4] The red, diamagnetic isomer[1,3,7] is a metal-metal bonded dimer,[8] $[(MeNC)_5Co\text{-}Co(CNMe)_5](ClO_4)_4$. Analogously, $[Co_2(CNEt)_{10}](ClO_4)_4$ has also been reported.[9] Only *t*-butylisocyanide has been observed to form a *tetrakis*(alkylisocyanide)cobalt(II) complex, $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, upon initial reaction with $Co(ClO_4)_2 \cdot 6H_2O$ in EtOH,[10] although sterically-hindered arylisocyanides form *tetrakis* complexes containing coordinated perchlorate ions, $[Co(CNR)_4(ClO_4)_2]$, R = 2,6-$Me_2C_6H_3$, 2,6-$Et_2C_6H_3$, 2,6-$(Me_2CH)_2C_6H_3$.[11-13]

This present work investigates reactions of $CNCHMe_2$ with $Co(ClO_4)_2 \cdot 6H_2O$ and $Co(BF_4)_2 \cdot 6H_2O$ in EtOH, and $CNCMe_3$ with $Co(BF_4)_2 \cdot 6H_2O$. This should establish whether $CNCHMe_2$ reacts analogously to CNMe and CNEt, or to $CNCMe_3$. This should also establish whether the ClO_4^- anion is critical in formation of a *tetrakis* complex, or if coordination is determined by the $CNCMe_3$ ligand.

EXPERIMENTAL

Reagents

Commercial alkylisocyanides (Strem), $CNCHMe_2$, $CNCMe_3$, CNC_4H_9-*n*, CNC_6H_{11}, were used without redistillation. Diethyl ether was filtered through an alumina column immediately before use.

Instrumentation

IR spectra were recorded on a Perkin Elmer 1710 FT-IR instrument. Solution electronic spectra were recorded on a Shimadzu UV-365. Diffuse reflectance spectra were recorded on a Cary Model 2390; powdered samples were measured relative to $BaSO_4$. Molar conductivities were measured on ~0.001 M samples at 25.0°C using a Crison 525 conductimeter. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey magnetic susceptibility balance. Effective magnetic moments were calculated assuming Curie Law behaviour. The C, H, N, and Cl analyses were performed commercially; Co was analyzed by atomic emission using a Spectroscan III DC argon plasma atomic emission spectrometer. Samples were digested in conc. nitric acid.

$[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$

A solution of 10.0 g $CNCHMe_2$ in 10.0 cm^3 of EtOH was added dropwise to a filtered, well-stirred solution of 10.6 g $Co(ClO_4)_2 \cdot 6H_2O$ (*i.e.*, 5:1 CNR:Co mole ratio) in 50 cm^3 of EtOH and chilled in ice. A dark blue solution resulted, but no precipitate was observed. The mixture was warmed to room temperature, then 75 cm^3 of ether was added in small aliquots, and the solution chilled to 0°C. Crystals formed within 30 min, but the solution was chilled overnight for complete precipitation. The mixture was filtered cold, separating maroon-red crystals from a green filtrate. The product was washed with two 20 cm^3 portions of ether and sucked dry in air. Yield: 14.7 g (78%). The product is hygroscopic and was stored under desiccation. Anal.: calc. for $Co_2C_{40}H_{70}Cl_4N_{10}O_{16} \cdot 5H_2O$: C, 37.05; H, 6.22; N, 10.80; Cl, 10.94; Co, 9.1%. Found: C, 36.74; H, 6.15; N, 10.94; Cl, 10.82; Co, 9.5%.

Characterization in solid state: melting range, 90–98°C (dec). IR: ν(O–H), 3380vw, 3530w, 3600w cm^{-1}; $\nu(-N\equiv C)$, 2018w, ~2120vw(sh), 2231vs(br), ~2253w(sh) cm^{-1} (nujol). Diffuse reflectance spectrum: ~784br (A = 0.64), ~500br (1.70), 396 (1.67), 344 (1.79), ~276 (1.63), 216 (1.49) nm. Magnetic susceptibility: $\chi_g = -380 \pm 25 \times 10^{-9}$ (cgs). Characterization in solution: $\nu(-N\equiv C)$, 2023w, ~2122vw, 2231vs cm^{-1} (CH_3NO_2); 2023w, 2119m, 2162m, ~2206m(sh), 2227vs cm^{-1} (CH_2Cl_2). Molar conductivity: 310 (CH_3CN), 195 (CH_3NO_2), 180 (acetone), 165 (CH_3OH) Ω^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\chi_g = 2.67 \pm 0.24 \times 10^{-6}$ (cgs), $\mu_{eff} = 2.21 \pm 0.08$ BM (CH_3CN); 2.48 ± 0.07 BM (CH_3NO_2); 2.89 ± 0.07 BM (CH_2Cl_2); 2.22 ± 0.07 BM ($CHCl_3$); 2.41 ± 0.04 BM (CF_3CH_2OH); 2.47 ± 0.07 BM ($CH_3C(O)C_2H_5$); 2.67 ± 0.06 BM (acetone). Solution concentrations are based on the monomeric formula, $[Co(CNCHMe_2)_5]X_2 \cdot 2.5H_2O$.

Analogous synthesis produced $[Co_2(CNCHMe_2)_{10}](BF_4)_4 \cdot 5H_2O$. Anal.: calc. for $Co_2C_{40}H_{70}B_4F_{16}N_{10} \cdot 5H_2O$: C, 38.55; H, 6.47; N, 11.24; Co, 9.5%. Found:

C, 38.73; H, 6.22; N, 11.44; Co, 9.9%. Characterization in solid state: melting range, 75–85°C (dec). IR: ν(O–H), 3385vw, 3560w, 3625w cm^{-1}; v(–N≡C), 2028vw, 2069w, 2236vs(br), ~2256w(sh) cm^{-1} (nujol). Electronic spectrum: ~817vbr (1.20), ~522vbr (1.65), ~483vbr (1.64), ~352vbr (1.62), ~282br (1.55), 219 (1.40) nm. Magnetic susceptibility: $\chi_g = -435 \pm 11 \times 10^{-9}$ (cgs). Characterization in solution: ν(–N≡C), 2018w, ~2120vw, 2233vs(br) cm^{-1} (CH_3NO_2); 2034w, 2119m, 2161m, 2229vs cm^{-1} (CH_2Cl_2). Molar conductivity: 300 (CH_3CN), 180 (CH_3NO_2), 165 (acetone), 145 (CH_3OH) Ω^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\chi_g = 2.0 \pm 0.7 \times 10^{-6}$ (cgs), $\mu_{eff} = 1.9 \pm 0.25$ BM (CH_3CN); 2.2 ± 0.3 BM (CH_3NO_2), 2.0 ± 0.1 BM (CH_2Cl_2); 2.0 ± 0.3 BM ($CHCl_3$).

$[Co(CNCMe_2)_3H_2O](BF_4)_2 \cdot 2.5H_2O$

A solution of 2.43 g $CNCMe_3$ in 2.5 cm^3 of EtOH was added dropwise to a filtered, well-stirred solution of 2.50 g $Co(BF_4)_2 \cdot 6H_2O$ (4:1 CNR:Co mole ratio) in 20 cm^3 of EtOH at 0°C. Intense blue-purple colour resulted on initial addition of $CNCMe_3$, but the solution was pale pink with a fine precipitate present when the addition was complete. The reaction mixture was warmed to room temperature, then the pale beige (flesh coloured) powder was filtered and sucked dry in air. Yield: 4.02 g (88%). Crude product was dissolved in 22 cm^3 of CH_3CN, filtered through cotton, and precipitated by addition of 40 cm^3 of ether. Yield: 3.01 g (75% recovery; 66% overall yield). The product is slightly hygroscopic and was stored under desiccation. Anal.: calc. for $CoC_{20}H_{38}B_2F_8N_4O \cdot 2.5H_2O$: C, 38.24; H, 6.90; N, 8.92; Co, 9.4%. Found: C, 37.85; H, 7.03; N, 9.14; Co, 9.4%.

Characterization in solid state: melting range, 104–107°C (dec). IR: v(O–H), 3500s, 3590s cm^{-1}; ν(–N≡C), 2035w, 2218vs cm^{-1} (nujol). Electronic spectrum: ~824br (0.218), ~522sh, 462 (0.241), 333 (0.692), ~285sh, 262 (1.52), 214 (1.30) nm. Magnetic susceptibility: $\chi_g = 3.12 \pm 0.07 \times 10^{-6}$ (cgs), $\mu_{eff} = 2.34 \pm 0.01$ BM. Characterization in solution: ν(–N≡C), 2022w, ~2209w(sh), 2225vs, ~2252vw(sh) cm^{-1} (CH_3NO_2). Molar conductivity: 340 (CH_3CN), 190 (CH_3NO_2), 220 (acetone), 195 (CH_3OH) Ω^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\chi_g = 4.90 \pm 0.30 \times 10^{-6}$ (cgs), $\mu_{eff} = 2.84 \pm 0.08$ BM (CH_3CN); 3.01 ± 0.07 BM (CH_3NO_2).

$[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was prepared as previously reported.[10] Characterization in solid state: IR: ν(O–H), 3430s, 3490m(sh) cm^{-1}; ν(–N≡C), 2032w, 2216vs, ~2222w(sh) cm^{-1} (nujol). Electronic spectrum: ~814br (0.289), ~525sh, 462 (0.338), 334 (0.858), ~276sh, 263 (1.54), 216 (1.32) nm. Magnetic susceptibility: $\chi_g = 3.74 \pm 0.07 \times 10^{-6}$ (cgs), $\mu_{eff} = 2.48 \pm 0.03$ BM. Characterization in solution: ν(–N≡C), 2024w, ~2206w(sh), 2225vs, ~2251vw(sh) cm^{-1} (CH_3NO_2). Molar conductivity, 320 (CH_3CN), 180 (CH_3NO_2), 180 (acetone), 175 (CH_3OH) Ω^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\chi_g = 5.25 \pm 0.31 \times 10^{-6}$ (cgs), $\mu_{eff} = 2.90 \pm 0.11$ BM (CH_3CN); 2.89 ± 0.04 BM (CH_3NO_2).

RESULTS AND DISCUSSION

Syntheses of the Complexes

Reaction of isopropylisocyanide with cobalt(II) is analogous to reactions of CNMe and CNEt, but not to $CNCMe_3$; a *tetrakis* complex with *t*-butylisocyanide can be prepared with BF_4^- as well as ClO_4^-. Reaction with *n*-butylisocyanide is analogous to that with isopropylisocyanide, but the complexes were not well-crystallized so characterization was not attempted. Reaction with cyclohexylisocyanide is also analogous, but the complexes are very soluble, the maroon crystals softening to a blue oil upon warming to room temperature. Thus $CNCMe_3$ appears unique for alkylisocyanides in forming *tetrakis* Co(II) complexes.

Solubility differences distinguish the $CNCHMe_2$ and $CNCMe_3$ complexes; $CNCHMe_2$ complexes are significantly more soluble in polar organic solvents. Solubility is crucial in the syntheses. $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ readily precipitate from ethanol solution. $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ require ether addition and extensive chilling for precipitation, and cold filtration without rinse to prevent redissolution. Complexes with CNC_6H_{11} are too soluble to crystallize from ethanol, and complexes with CNC_4H_9-*n* become intractable after precipitation. $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ species are recrystallized from CH_3CN, C_2H_5CN, or CH_3NO_2 and ether, while recrystallization of $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ is difficult and unsatisfactory; freshly-prepared samples were characterized.

Characterization in the Solid State

Diffuse reflectance electronic spectra for the complexes (see Figure 1) are reasonable for tetragonal or five-coordinate Co(II); tetrahedral geometry is excluded. Spectra

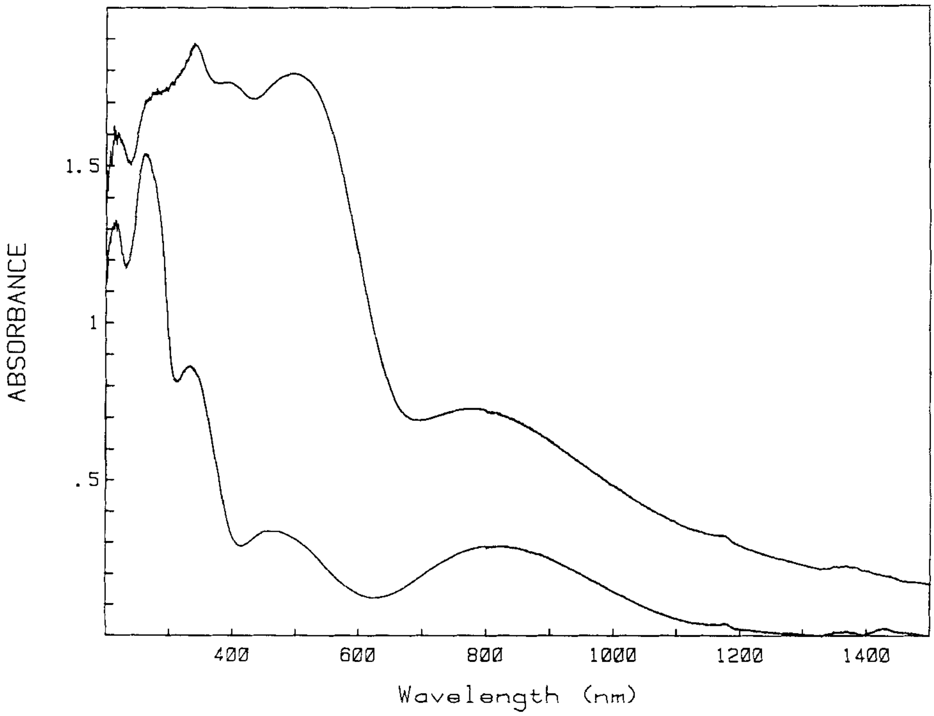

FIGURE 1 Diffuse reflectance electronic spectra for $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ (top) and $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ (bottom).

for $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ and $[Co_2(CNMe)_{10}](ClO_4)_4$ (Ref. 4) are very similar, so an analogous structure is suggested. Spectra for the $CNCHMe_2$ and $CNCMe_3$ complexes are quite similar, as expected for pseudo-octahedral and square pyramidal Co(II) with the same ligands.

Magnetic susceptibilities indicate one-electron paramagnetism for $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$. This is reasonable for square pyramidal or square planar coordination of strong field ligands; tetrahedral coordination is excluded. $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ complexes are diamagnetic when freshly prepared, becoming paramagnetic with age. Measured diamagnetism is in reasonable agreement with calculated values (Table I and literature[14]); $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$, $\chi_M = -500 \pm 32 \times 10^{-6}$, -678×10^{-6}; $[Co_2(CNCHMe_2)_{10}](BF_4)_4 \cdot 5H_2O$, $\chi_M = -540 \pm 13 \times 10^{-6}$, -686×10^{-6} (cgs). Diamagnetism supports a proposed dimeric structure with a direct Co–Co bond, $[(Me_2HCNC)_5Co\text{–}Co(CNCHMe_2)_5]X_4 \cdot 5H_2O$.

The $\nu(-N \equiv C)$ patterns of one broad band with shoulders suggests slightly different RNC ligands, bridging RNC being excluded. Frequencies of the strong bands, 2231, 2236 cm^{-1} ($CNCHMe_2$) (2216, 2218 ($CNCMe_3$)) shift to higher energy relative to the free ligand (2144, 2136 cm^{-1}, respectively), indicating coordinated RNC provides more σ-donation than π^*-acceptance, as expected in Co(II) complexes. The $\nu(ClO_4)$ and $\nu(BF_4)$ modes are normal for symmetrical anions, so ClO_4^- coordination is excluded. The doubled $\nu(O\text{–}H)$ band in $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is suggestive of a coordinated water molecule. The $\nu(O\text{–}H)$ stretches in $[Co(CNCMe_3)_4H_2O](BF_4)_2 \cdot 2.5H_2O$ are stronger and widely separated, suggesting coordinated and non-coordinated water molecules.

The structure of $[Co(CNCMe_3)_4H_2O](BF_4)_2 \cdot 2.5H_2O$ is almost certainly analogous to that of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, with extra water molecules being non-coordinated. One H_2O molecule is presumably coordinated; four coordination is not expected.[15,16] The most probable structure is square pyramidal $[Co(CNCMe_3)_4H_2O]^{2+}$, with H_2O in the apical position. The $CNCMe_3$ ligand, not the ClO_4^- anion, is determinative in formation of *tetrakis*(alkylisocyanide)-cobalt(II) complexes. Structures for $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ are almost certainly analogous to each other, and probably involve a Co–Co bond without bridging CNR.

TABLE I
Measured diamagnetic susceptibilities

Formula	$\chi_g \times 10^9$	$\chi_M \times 10^6$
$CNCHMe_2$	-664 ± 9	-45.9 ± 0.6
$CNCMe_3$	-647 ± 11	-53.8 ± 0.9
$NaBF_4$	-372 ± 7	-40.9 ± 0.8
CH_3CN	-624 ± 14	-25.6 ± 0.6
CH_3NO_2	-327 ± 6	-19.9 ± 0.4
CH_2Cl_2	-528 ± 12	-44.9 ± 1.0
$CHCl_3$	-467 ± 11	-55.7 ± 1.3
CF_3CH_2OH	-411 ± 11	-41.1 ± 1.1
$CH_3C(O)CH_3$	-543 ± 8	-31.5 ± 0.5
$CH_3C(O)C_2H_5$	-574 ± 14	-41.4 ± 1.0

Characterization in Solution

The Co–Co bond proposed in $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ dissociates in solution; no evidence suggests dimer$\rightleftharpoons$monomer equilibrium. Molar conductivities in CH_3CN, CH_3NO_2, $CH_3C(O)CH_3$, and CH_3OH for all complexes are appropriate for fully dissociated 2:1 electrolytes.[17] The solubilities and Λ_M values attest to dissociation of the $CNCHMe_2$ complexes; a 4:1 salt should have limited solubility and show significant ion-pairing.

The $\nu(-N{\equiv}C)$ bands for $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ in CH_3NO_2 are effectively identical, with one strong band at 2225 cm^{-1}; the $\nu(-N{\equiv}C)$ for $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ in CH_3NO_2 is strong at 2231, 2233 cm^{-1}. These frequencies are appropriate for Co(II) complexes. IR spectra in CH_2Cl_2 show a strong band at 2227, 2229 cm^{-1}; and a 2119, 2161–2162 cm^{-1} pattern indicative of $[Co(CNR)_5]X$.[18,19] The $\nu(-N{\equiv}C)$ modes for $[Co(CNR)_5]^+$ are extremely intense, so only slight reduction has probably taken place in solution.

Mass susceptibilities for the complexes in 3–10% by weight solution were calculated $\left(\chi_g = \left(\frac{m_1 + m_0}{m_1}\right)\chi_{solution} - \left(\frac{m_0}{m_1}\right)\chi_0\right)$ using measured susceptibilities (χ_0) for the solvents (Table I). Effective magnetic moments (μ_{eff} = 2.85–3.0 BM) for $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ are in the upper range expected for low-spin

TABLE II

Solution electronic spectroscopic data for $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ and $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$

Solvent	Electronic spectrum[a]
	$[Co(CNCMe_3)_4H_2O](ClO_4)_2$
CF_3CH_2OH	835 (225), 460 (35), 320 (360), 265 (2800), 225 (5500)*
CH_3NO_2	820 (200), ~430sh (70)
CH_3CN	745 (92), ~460sh (25), ~320sh (320), ~275sh (1400), 240 (4300)*
CH_3OH	675 (51), ~510sh (16)
	$[Co(CNCMe_3)_4H_2O](BF_4)_2 \cdot 2.5H_2O$
CF_3CH_2OH	844 (250), ~436sh (110), 316 (540), 265 (2900), 223 (5800)*
CH_3NO_2	817 (240), ~444sh (100)
CH_3CN	730 (96), ~455sh (61), 320 (350), 273sh (1400), 239 (3900)*
CH_3OH	665 (86), ~290sh, 260 (1100), 230 (1400)*
	$[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$
CF_3CH_2OH	835 (260), 455 (40), ~308sh (680), 265 (3600), 222 (6500)*
CH_3NO_2	820 (290), ~440sh (62)
CH_2Cl_2	760 (200), ~430sh (48), 265 (4200), 230 (6200)*
$CH_3C(O)CH_3$	745 (180), ~435sh (46)
CH_3CN	745 (108), ~440sh (40), 260sh (2800)
CH_3OH	680 (128)
	$[Co_2(CNCHMe_2)_{10}](BF_4)_4 \cdot 5H_2O$
CF_3CH_2OH	845 (260), 455 (38), 283 (5700), 267 (5600), 222 (6400)*
CH_3NO_2	825 (260), ~460sh (44)
CH_2Cl_2	810 (235), 468 (38), 283 (5500), 271 (5600), 231 (5500)*
$CH_3C(O)CH_3$	765 (195), ~476sh (32), 329 (1300)
CH_3CN	745 (115), 276br (2400), 240 (4500)
CH_3OH	675 (135), ~279sh (1800), ~248sh (2000)

[a] The $\lambda_{max}(\varepsilon)$ in nm (m^{-1} cm^{-1}) without Gaussian resolution.

* Possible solvent interference.

Co(II),[14] but still indicative of one unpaired electron rather than three ($\mu_{eff} = 4.30$–5.20 BM[14]). The μ_{eff} values for $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$ (1.90–2.90 BM) are also within the range expected for low-spin Co(II).[14]

Solution electronic spectra are summarized in Table II. Decreasing λ_{max} and ε for the first band with increasing solvent coordinating ability is observed. In non-coordinating solvents (CF_3CH_2OH, CH_3NO_2), producing olive-green solutions, square pyramidal $[Co(CNCHMe_2)_5]^{2+}$ and $[Co(CNCMe_3)_4H_2O]^{2+}$ (with expected high ε) are probably present, although $[Co(CNCHMe_2)_5H_2O]^{2+}$ and $[Co(CNCMe_3)_4]^{2+}$ cannot be excluded. In coordinating solvents (CH_3CN, CH_3OH), giving blue solutions, pseudo-octahedral $[Co(CNCHMe_2)_5S]^{2+}$ and *trans*-$[Co(CNCMe_3)_4S_2]^{2+}$ can be expected. Spectra for $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ in CH_3OH are similar to diffuse reflectance spectra of $[Co(CNCMe_3)_4L_2](ClO_4)_2 \cdot nH_2O$, L = C_5H_5N, 3-MeC_5H_4N, 4-MeC_5H_4N, $C_5H_{10}NH$, $HN(CH_2CH_2)_2O$.[20] In solvents of intermediate coordinating ability (CH_2Cl_2, acetone), showing bluegreen solutions, ClO_4^- and BF_4^- salts show greatest differences, so formation of $[Co(CNCHMe_2)_5S]^{2+}$ may be incomplete.

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