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Synthesis of paramagnetic tetrakis(benzylisocyanide)bis(tri-*p*-tolylarsine oxide)cobalt(III) tetrafluoroborate. An example of oxidation of ligand and metal in reaction of pentakis(arylisocyanide)cobalt(II) with triarylarsine

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Abstract

Golden yellow, paramagnetic $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ is synthesized by reaction of $[Co(CNCH_2Ph)_5](BF_4)_2$ with excess $As(C_6H_4Me\text{-}p)_3$ in CH_2Cl_2 solution. Both AsR_3 and Co(II) are apparently rapidly oxidized in this novel reaction, although Co(II) disproportionation has not been excluded. The microcrystalline salt is characterized by IR, electronic spectra, magnetic susceptibility and molar conductivity; stability in solution is limited. Effective magnetic moment of 3.58 BM indicates the intermediate spin state of two unpaired electrons, previously unobserved for Co(III). Simple crystal field rationalization suggests a $^3B_{2g}[(e_g)^4(b_{2g})^1(a_{1g})^1]$ ground state, based on tetragonally elongated octahedral coordination. $[Co_2(CNCH_2Ph)_{10}](BF_4)_4\cdot H_2O$ is synthesized as starting material and characterized; data are consistent with Co–Co bonded dimeric structure in the solid state and $[Co(CNCH_2Ph)_5](BF_4)_2$ monomeric structure in solution.

Introduction

Spontaneous reduction of Co(II) to Co(I) characterizes many reactions with organoisocyanide ligands. The RNC, $R = p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$, $p\text{-}IC_6H_4$, themselves, in reaction with $CoX_2\cdot 6H_2O$ ($X = ClO_4$, BF_4), produce mixtures of pentakis(arylisocyanide)cobalt(I) and cobalt(II) complexes [1, 2]. Reaction of triarylphosphines with pentakis(arylisocyanide)cobalt(II) [3–8], $[Co(CNCMe_3)_4H_2O)](ClO_4)_2$ [9] and $[Co_2(CNCHMe_2)_{10}]X_4\cdot 5H_2O$ [10] produce disubstituted Co(I) complexes, $[Co(CNR)_3(PR_3)_2]X$. Reaction of trialkylphosphines leads to a greater variety of products. Reactions with arylisocyanide–Co(II) complexes produce both disubstituted and monosubstituted Co(I) complexes, $[Co(CNR)_4PR_3]X$, depending on the arylisocyanide and trialkylphosphine [11]. Reaction with $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ produced only disubstituted Co(I) complexes [9, 10], while reaction with $[Co_2(CNCHMe_2)_{10}]X_4\cdot 5H_2O$ produced $[Co(CNR)_3(PR_3)_2]X$ with $PR_3 = P(CH_2Ph)_3$, $P(C_2H_4CN)_3$, $P(NMe_2)_3$, and Co(III) complexes, $[Co(CNR)_4(PR_3)_2]X_3$, with $PR_3 = P(C_6H_{13}\text{-}n)_3$, $P(C_4H_9\text{-}n)_3$ [10]. The disproportionation nature of this latter reaction was established by synthesis of $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$ and $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ in reaction of $[Co(CNC_6H_{11})_5](ClO_4)_2$ with $P(C_6H_{13}\text{-}n)_3$ [12]. $[Co(CNR)_4(PR_3)_2]X_3$, $X = ClO_4$, BF_4; $CNR = CNCHMe_2$, CNC_6H_{11}, $CNC_4H_9\text{-}n$, $CNCH_2Ph$; $PR_3 = P(C_6H_{13}\text{-}n)_3$, $P(C_4H_9\text{-}n)_3$, $P(C_3H_7\text{-}n)_3$; have been reported [13].

Reaction of triphenylarsine with $[Co(CNPh)_5](ClO_4)_2\cdot H_2O$ achieved reduction/ligand-substitution in producing $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ [14], but in reaction with $[Co(CNC_6H_3Me_2\text{-}2,6)_5]X_2\cdot 0.5H_2O$, only $[Co(CNR)_4(ClO_4)_2]$ and $[Co(CNR)_5]BF_4$ were produced [15]. Reaction of triarylarsines, AsR_3 ($R = Ph$, $C_6H_4Me\text{-}p$), with pentakis(alkylisocyanide)cobalt(II) has produced disubstituted Co(II) complexes, $[Co(CNR)_4(AsR_3)_2]X_2$ [16]; so the synthesis reported in this paper is unique, involving oxidation, not reduction, and oxidation of both ligand and Co(II).

Experimental

Commercial benzylisocyanide and tri-*p*-tolylarsine (Strem) were used without purification. Anhydrous diethyl ether was filtered through alumina immediately before use. IR spectra were recorded on a Mattson Polaris FT-IR. Solution electronic spectra were recorded on a Shimadzu UV-365; diffuse reflectance spectra were measured on a Cary model 2390 or an Integrating

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Sphere attachment to the Shimadzu UV-365. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey magnetic susceptibility balance. Molar conductivities were measured on ~0.001 M solutions at 25.0 °C using a Crison model 525 conductimeter. The C, H and N elemental analyses were performed using a Carlo Erba CHN-O/S elemental analyzer, model 1106. Microsamples were weighed on a Sartorius Ultramicro electrobalance.

Synthesis of $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$

A solution of 2.34 g $CNCH_2Ph$ in 2.5 ml EtOH was added dropwise to a filtered, well-stirred solution of 1.50 g $Co(BF_4)_2 \cdot 6H_2O$ (i.e. 5:1.1 CNR:Co mole ratio) dissolved in 7.0 ml EtOH and chilled in ice. Initial drops produced a red–brown solid which became progressively maroon–red as reaction continued. When addition was complete, the mixture was warmed to room temperature, and the dark maroon, crystalline product was filtered from the dark green solution, washed with 3.0 ml cold EtOH, and dried under suction/air. Yield 2.88 g (88%). *Anal.* Calc. for $Co_2C_{80}H_{72}B_4F_{16}N_{10}O$: C, 58.07; H, 4.39; N, 8.47. Found: C, 58.11; H, 4.34; N, 8.40%.

Characterization in solid state: melting range, 94–100 °C (dec.). IR: ν(O–H), ~3630w, ~3555vw cm^{-1}; $\nu(-N{\equiv}C)$, 2247vs, 2205s cm^{-1} (Nujol). Electronic spectrum: ~825br ($A = 0.60$), ~495br,sh (1.66), ≈385vbr (1.70), ~280br (1.58), 223 (1.34) nm. Magnetic susceptibility: $\chi_g = -250 \pm 14 \times 10^{-9}$, $\chi_M = -410 \pm 23 \times 10^{-6}$ (cgs). Characterization in solution: $\nu(-N{\equiv}C)$: 2245vs, 2175w, 2136w cm^{-1} (CH_3NO_2); 2241vs, 2173w, 2136m cm^{-1} (CH_2Cl_2). Electronic spectra: 810(235), ≈280sh(5900), 267sp(6400), 263sp(6600), 257sp(6800), 250sp(7000) nm (CH_2Cl_2); 697(110), ≈285sh(2500), 267sp(3400), 263sp(3700), 257sp(3800), ~251sh(4000), 241(5400) nm (CH_3CN). Molar conductivity: 275 (CH_3CN), 170 (acetone), 170 (CH_3NO_2), 160 (CH_3OH), 14 (CH_2Cl_2) Ω^{-1} cm^2 mol^{-1}.

Synthesis of $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$

A 700 mg sample of $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ was dissolved in 4.5 ml CH_2Cl_2, filtered through cotton, and chilled in ice. Then 740 mg $As(C_6H_4Me\text{-}p)_3$ (solid; 1:2.5 Co:As mole ratio) was slowly added while the reaction mixture was stirred. Dropwise addition of 5.5 ml ether caused initial precipitation of a golden-yellow solid. A total of 8.5 ml ether was added, and the solid was filtered without chilling in ice. The golden-yellow microcrystalline product was washed twice with 2.5 ml portions of ether, and dried under suction/air. Upon overnight refrigeration, a second crop of the golden-yellow product was recovered from the dark green filtrate. Crude product (425 mg; 50% yield based on BF_4; 33% based on Co) was recrystallized from CH_2Cl_2/ether; yield 270 mg (64% recovery; 32% overall yield). *Anal.* Calc. for $CoC_{74}H_{70}As_2B_3F_{12}N_4O_2$: C, 58.61; H, 4.65; N, 3.69. Found: C, 58.78; H, 4.68; N, 3.67%.

Characterization in solid state: melting range, 180–188 °C (dec.). IR: $\nu(-N{\equiv}C)$, 2258vs, ~2219w(sh) cm^{-1}; $\nu(As{=}O)$, 818m cm^{-1} (Nujol). Electronic spectrum: ~640sh (0.04), ~460sh (1.07), ~380br (1.11), ~270sh (1.07) nm. Magnetic susceptibility: $\chi_g = 3040 \pm 25 \times 10^{-9}$ (cgs), $\mu_{eff} = 3.58 \pm 0.01$ BM. Characterization in solution: $\nu(-N{\equiv}C)$, 2233s, 2172m, 2135s cm^{-1} (CH_2Cl_2); 2242sh, 2232s, 2175w, 2133m cm^{-1} (CH_3NO_2); 2228s, 2199m, 2193m cm^{-1} (CF_3CH_2OH). Electronic spectra: ~640sh(15), 441(13000), ~370br,sh(5500), 279(10000), ~250sh(14000), 225sh(52000) nm (CH_3CN); ~825br(68), 415sh(800), ≈285sh(6400), ~240br(14000) nm (CH_2Cl_2); ~890br(200), ≈490sh(640), ≈390sh(2600), 318(5700), ~260(6100), ~254(6800), 228(72000) nm (CF_3CH_2OH). Molar conductivity: 460 (CH_3CN), 230 (CH_3NO_2), 22 (CH_2Cl_2) Ω^{-1} cm^2 mol^{-1}.

Results and discussion

Synthesis of the complexes

Preparation of $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ is analogous to the synthesis of $[Co_2(CNCHMe_2)_{10}]X_4 \cdot 5H_2O$, X = ClO_4, BF_4 [17], except that addition of ether is not required for precipitation from EtOH. Like other reported alkylisocyanide–Co(II) complexes, with CNR = CNMe [18], CNC_2H_5 [19], $CNCHMe_2$, CNC_4H_9-n [17], except complexes with $CNCMe_3$ [9, 17], this complex is most probably dimeric in the solid state, $[(PhCH_2NC)_5Co\text{-}Co(CNCH_2Ph)_5](BF_4)_4 \cdot H_2O$, with a monomeric cation in solution, $[Co(CNCH_2Ph)_5]^{2+}$. Measured diamagnetism ($-410 \pm 20 \times 10^{-6}$ cgs) is less than that calculated for diamagnetic correction of the ligands (-853×10^{-6} cgs), however, and the complex gradually becomes paramagnetic upon prolonged storage. In solution there is evidence of slight reduction to Co(I). The perchlorate analog, $[Co_2(CNCH_2Ph)_{10}](ClO_4)_4 \cdot 2.5H_2O$ (*Anal.* Calc. C. 55.47; H, 4.36; N, 8.09. Found C, 55.24; H, 4.38; N, 8.12%) is synthesized analogously but is less stable in solution and in the solid state.

Synthesis of $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ by reaction of excess $As(C_6H_4Me\text{-}p)_3$ with $[Co(CNCH_2Ph)_5](BF_4)_2$ in CH_2Cl_2 solution is a very interesting, if not novel, reaction. Slow ligand oxidation, AsR_3 to $OAsR_3$, has been observed in reactions with $[Co(CNCHMe_2)_5](ClO_4)_2$ [16], but this oxidation is rapid, and apparently oxidizes both AsR_3 and Co(II). Disproportionation of Co(II) has not been excluded, but in the absence of any indication of a Co(I) product, this reaction is being considered as oxidation. Yield is relatively low (50% as crude product; 32% recrystallized), but this may be due to solution instability of the complex. Aged solution samples eventually revert to the dark blue (tetrahedral) complex, $[Co\{OAs(C_6H_4Me\text{-}p)_3\}_4](BF_4)_2$.

Characterization of $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$

The $\nu(\text{-N}{\equiv}C)$ and $\nu(As{=}O)$ are the important features in the IR spectrum. The $\nu(\text{-N}{\equiv}C)$ frequency (2258 cm^{-1}) is rather low for Co(III), but this is compatible with $OAsR_3$ being strongly σ-donating with no π^*-accepting ability. The $\nu(\text{-N}{\equiv}C)$ pattern (see Fig. 1) is typical of four approximately square planar organoisocyanides, as in $[Co(CNR)_4(ClO_4)_2]$ [15, 20, 21] or $[Co(CNCMe_3)_4L_2](ClO_4)_2$ [22]. Slight distortion from D_{4h} symmetry for *trans*-$[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ probably takes place in the solid state. The $\nu(As{=}O)$ was deduced by comparing the IR spectrum with those for AsR_3, $[Co_2(CNR)_{10}](BF_4)_4 \cdot H_2O$ and Nujol. A medium-intensity, sharp band at 818 cm^{-1} was thereby assigned as $\nu(As{=}O)$. This represents a rather large shift to lower frequency (62 cm^{-1}, compared to usual *c.* 35), relative to the free ligand (880 cm^{-1}) [23].

The diffuse reflectance electronic spectrum is not very diagnostic. The low-intensity, low-energy band ~640 nm is probably d–d in nature, and could represent a spin-forbidden transition. Other bands are probably charge transfer. Magnetic susceptibility leading to an effective (Curie Law) magnetic moment of 3.58 BM most probably represents an intermediate spin state of two unpaired electrons ($\mu_{so} = 3.83$ BM), instead of the usual Co(III) diamagnetic low-spin state or a high-spin state of four unpaired electrons ($\mu_{so} = 4.90$ BM). High-spin K_3CoF_6 (which along with $Co(H_2O)_3F_3$ seem to be the only high-spin Co(III) complexes known) is reported to have $\mu_{eff} = 4.26$ BM [24]. Green Co(III) complexes, $[C_5H_5Co\{(RO)_2PO\}_3Co\{(RO)_2PO\}_3CoC_5H_5]X$, $X = PF_6$, ClO_4, have $\mu_{eff} = 2.6$ BM at 300 K in $CHCl_3$ solution [25]. Since μ_{eff} increases steadily to 4.1 BM at 393 K in the solid state, this system is considered a temperature-dependent equilibrium between high-spin and low-spin states, rather than the intermediate-spin state. Thus $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ may be the first example of a six-coordinate Co(III) complex with two unpaired electrons.

Characterization of $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ in solution must be interpreted cautiously. Molar conductivity in CH_3NO_2 is appropriate for 3:1 electrolyte behavior, and the value in CH_3CN is slightly high [26]. Λ_M in CH_2Cl_2 shows ion-pairing, as expected. The sample decomposes in acetone. The $\nu(\text{-N}{\equiv}C)$ patterns in CH_3NO_2 and CH_2Cl_2 suggest the $[Co(CNR)_5]^+$ species (2175, 2172m; 2133, 2135s cm^{-1}), while in CF_3CH_2OH a Co(II) species (2199, 2193w cm^{-1}), may be present, in addition to the expected Co(III) species. The $\nu(\text{-N}{\equiv}C)$ for $[Co(CNR)_5]^+$ are extremely intense, so only a small concentration of Co(I) is probably formed in solution.

Electronic spectra (~10^{-3} to 10^{-4} M) rapidly change with time; solution stability appears to be $CH_3CN > CH_2Cl_2 > CF_3CH_2OH$. In CH_3CN, the initial spectrum is similar to the solid state: a weak ($\epsilon \simeq 15$) CF, possibly spin-forbidden, band ~640 nm and charge-transfer bands beyond 440 nm. In time, a broad band develops ~700 nm; this and the first reported band in CH_2Cl_2 and CF_3CH_2OH are probably due to a Co(II) species rapidly formed in solution. Samples in CH_2Cl_2 and CH_3CN eventually become dark blue with the unmistakable pattern indicative of the tetrahedral species, $[Co\{OAs(C_6H_4Me\text{-}p)_3\}_4]^{2+}$ [27].

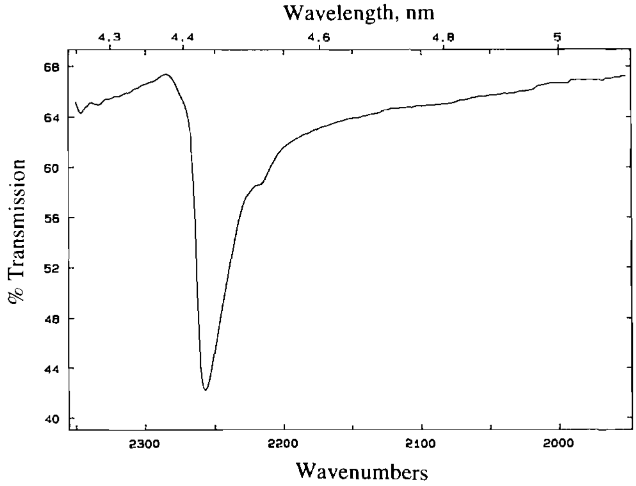

Fig. 1. The $\nu(\text{-N}{\equiv}C)$ IR pattern for $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ (in Nujol).

Significance of the magnetic moment

Paramagnetic ground state for $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ seems at first surprising, in view of the clearly strong field nature of organoisocyanide ligands albeit the weak field nature of $OAsR_3$. Paramagnetism probably results not from the crystal field strengths of the ligands, however, but from the particular CF splitting pattern for the partially filled d-orbitals. Rather than viewing this complex as approximately octahedral, in which case it should certainly be diamagnetic not high-spin, it is better to consider this geometry as an extreme tetragonal elongation of the octahedron [28]. The $OAsR_3$ are much weaker ligands than CNR, so this coordination may in fact be more closely approximated as square planar than octahedral. In this CF pattern (see Fig. 2), two-electron paramagnetism should result whenever the $a_{1g}(d_{3z^2-r^2})$

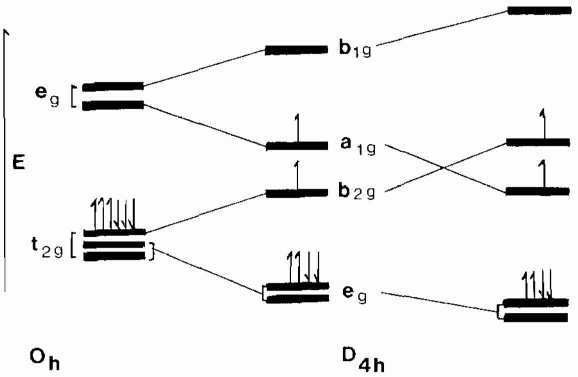

Fig. 2. Crystal field splitting diagram for progressive tetragonal elongation of octahedral coordination suggested for intermediate-spin Co(III).

and $b_{2g}(d_{xy})$ levels are in reasonably close proximity (when CFSE is less than the electron-pairing energy). The proposed ground-state electronic configuration for $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ is thus $^3B_{2g}$, whether this arises from the $(e_g)^4(b_{2g})^1(a_{1g})^1$ or $(e_g)^4(a_{1g})^1(b_{2g})^1$ configuration. Further investigation is needed to confirm this configuration.

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