Synthesis of tetrakis(cyclohexylisocyanide)bis(tri-n-hexylphosphine)-cobalt(III) perchlorate and tris(cyclohexylisocyanide)bis(tri-n-hexylphosphine)cobalt(I) perchlorate. An example of cobalt(II) disproportionation with alkylisocyanide and trialkylphosphine ligands

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Abstract

Isolation of $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ and $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ in the reaction of $[Co(CNC_6H_{11})_5](ClO_4)_2$ with excess $P(C_6H_{13}\text{-n})_3$ in ethanol solution establishes the disproportionation nature of this reaction: $2[Co(CNR)_5]^{2+} + 4PR_3 \rightarrow [Co(CNR)_3(PR_3)_2]^+ + [Co(CNR)_4(PR_3)_2]^{3+} + 3CNR$. The complexes are characterized by $\nu(-N{\equiv}C)$, electronic spectra, magnetic susceptibility and molar conductivity. White, diamagnetic $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ is probably a regular tetragonal structure (D_{4h}) in solution but distorted in the solid state, i.e. *trans*-$[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$. Yellow, diamagnetic $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ is probably distorted axially disubstituted trigonal bipyramidal (C_{2v}) in both solution and the solid state. Molar conductivities for $[Co(CNC_6H_{11})_3\text{-}P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ indicate fully-ionized 1:1 electrolyte behavior in all solvents, but Λ_M values for $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ suggest 3:1 electrolyte behavior in CH_3CN and CH_3NO_2, with increasing ion-pairing in Me_2NCHO, CF_3CH_2OH, acetone and CH_2Cl_2.

Introduction

Reaction of $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ ($X = ClO_4$, BF_4) with unsubstituted trialkylphosphines, $P(C_4H_9\text{-n})_3$ and $P(C_6H_{13}\text{-n})_3$, to yield cobalt(III) complexes, $[Co(CNCHMe_2)_4(PR_3)_2]X_3$ [1], was postulated to be Co(II) disproportionation, but has not been established. Disproportionation reactions of Co(II) with tertiary phosphorus ligands have been observed with trialkylphosphites, $2Co(ClO_4)_2 + 11P(OR)_3 \rightarrow [Co\{P(OR)_3\}_6](ClO_4)_3 + [Co\{P(OR)_3\}_5]ClO_4$ [2–4]. This present work confirms the disproportionation reaction with trialkylphosphines.

Experimental

Commercial cyclohexylisocyanide (Fluka) and tri-n-hexylphosphine (Strem) were used without purification. Anhydrous diethyl ether was filtered through an alumina column immediately before use. IR spectra were recorded on a Mattson Polaris FT-IR. Solution electronic spectra were recorded on a Shimadzu UV-365. Magnetic susceptibilities were measured using a Johnson Matthey magnetic susceptibility balance. Melting ranges were measured in capillaries using an Electrothermal melting point apparatus. Molar conductivities were measured on ~0.001 M solutions at 25.0 °C using a Crison model 525 conductimeter with an Ingold flow-through cell. 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 $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ *and* $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$

A solution of 670 mg $Co(ClO_4)_2 \cdot 6H_2O$ dissolved in 3.0 ml EtOH and filtered through cotton with 0.5 ml EtOH rinse was chilled in ice. Then 1.000 g $C_6H_{11}NC$ (neat) was added dropwise while the

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Co(II) solution was stirred. The solution turned from pink to dark blue, but no solid precipitated. Next 2.620 g $P(C_6H_{13}\text{-n})_3$ (neat) was added dropwise while the reaction mixture was stirred. The colour of the solution changed to bright yellow while phosphine was being added, and a light yellow solid precipitated. The reaction mixture was allowed to stand 10 min at room temperature, then 5.0 ml ether was added dropwise and the solution chilled for 60 min. A white powder (1.123 g; 45% yield) was filtered from the yellow solution and washed twice with 2.0 ml portions of ether. The crude product was dissolved in 3.5 ml CH_3CN; the addition of 9.5 ml ether effected the initial precipitation. The total volume of ether added was 30.0 ml, and the solution was chilled thoroughly. Pure white microcrystals were filtered from the pale yellow solution. Addition of excess ether afforded a second crop. Yield: 1.049 g (93% recovery; 42% overall yield). *Anal.* Calc. for $CoC_{64}H_{122}Cl_3N_4O_{12}P_2$: C, 56.24; H, 9.00; N, 4.10. Found: C, 56.26; H, 9.12; N, 3.90%.

Characterization in the solid state: melting range, 150–155 °C (dec.); $\nu(-N{\equiv}C)$: 2240 vs, ~2208vw(sh), ~2022vw cm^{-1} (nujol). Magnetic susceptibility: $\chi_g = -300 \pm 20 \times 10^{-9}$, $\chi_M = -410 \pm 30 \times 10^{-6}$ cgs. Characterization in solution: $\nu(-N{\equiv}C)$: 2235vs cm^{-1} (CH_3NO_2), 2238vs cm^{-1} (CH_2Cl_2). Electronic spectra: 297.5 nm ($\epsilon = 33\,600$; CH_3CN), 297.5 nm (32 800; CH_2Cl_2). Molar conductivity: 340 (CH_3CN), 125 (acetone), 200 (CH_3NO_2), 165 (Me_2NCHO), 5.7 (CH_2Cl_2), 28 (CF_3CH_2OH) Ω^{-1} cm^2 mol^{-1}.

To the filtrate from the $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ synthesis, 35 ml ether was added slowly and the solution chilled overnight. Pale yellow crystals were filtered from the bright yellow solution and washed twice with 3.0 ml portions of ether. The addition of 40 ml ether and extensive refrigeration afforded a second crop. Partial evaporation, addition of more ether, and extensive refrigeration produced a third crop of yellow crystals. Yield: 655 mb (34%). The crude product was recrystallized from 1.5 ml CH_2Cl_2 and 50 ml ether. Yield: 452 mg (69% recovery; 23% overall yield). *Anal.* Calc. for $CoC_{57}H_{111}ClN_3O_4P_2$: C, 64.66; H, 10.57; N, 3.97. Found: C, 64.74; H, 10.73; N, 3.77%.

Characterization in the solid state: melting range, 104–109 °C (dec.); $\nu(-N{\equiv}C)$: ~2094w(sh), 2062s, 2040s cm^{-1} (nujol). Magnetic susceptibility: $\chi_g = -525 \pm 20 \times 10^{-9}$, $\chi_M = -560 \pm 20 \times 10^{-6}$ cgs. Characterization in solution: $\nu(-N{\equiv}C)$: ≈2072w(sh), 2059s, ≈2045w(sh) cm^{-1} (CH_3NO_2); ≈2070w(sh), 2057s, ≈2046w(sh) cm^{-1} (CH_2Cl_2). Electronic spectra: 279 ($\epsilon = 12\,100$), 237 (28 800) nm (CH_3CN); 278 (13 900), 237 (35 500) nm (CH_2Cl_2). Molar conductivity: 135 (CH_3CN), 130 (acetone), 84 (CH_3NO_2), 64 (Me_2NCHO), 57 (CH_2Cl_2), 27 (CF_3CH_2OH) Ω^{-1} cm^2 mol^{-1}.

Results and discussion

Significance of the syntheses

Isolation of the Co(I) species, $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$, as well as the Co(III) species, $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$, clearly establishes the disproportionation nature of this reaction: $2[Co(CNR)_5]^{2+} + 4PR_3 \rightarrow [Co(CNR)_3(PR_3)_2]^+ + [Co(CNR)_4(PR_3)_2]^{3+} + 3CNR$. Subsequent work has established an analogous disproportionation reaction of $[Co(CNC_6H_{11})_5]^{2+}$ with $P(C_4H_9\text{-n})_3$ and $P(C_3H_7\text{-n})_3$ [5]; and sole isolation of the Co(III) complexes, $[Co(CNR)_4(PR_3)_2]X_3$, $X = ClO_4$, BF_4; $CNR = CNC_4H_9\text{-n}$, $CNCH_2Ph$; $PR_3 = P(C_6H_{13}\text{-n})_3$, $P(C_4H_9\text{-n})_3$, $P(C_3H_7\text{-n})_3$ [5]; in reactions analogous to $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ reacted with $P(C_4H_9\text{-n})_3$ and $P(C_6H_{13}\text{-n})_3$ [1]. In view of the strong similarities, it is probably reasonable to conclude that all of these reactions involve disproportionation of the Co(II)–alkylisocyanide complex, but only in the case of CNC_6H_{11} has it been possible to isolate the Co(I) derivative. Predictions of high solubility and low stability for $[Co(CNR)_3(PR_3)_2]ClO_4$ [1] have also been confirmed.

What is most significant about these disproportionation reactions is the subtle chemical differences controlling reduction and disproportionation. Changing the alkylisocyanide from $CNCMe_3$ to $CNCHMe_2$ or CNC_6H_{11}, or changing substituted trialkylphosphines ($R = CH_2Ph$, CH_2CH_2CN, NMe_2) to unsubstituted ($R = C_4H_9\text{-n}$, $C_6H_{13}\text{-n}$), changes Co(II) → Co(I) reduction to Co(II) disproportionation. Chemical factors distinguishing these two reactions must be in a delicate balance. Unfortunately neither mechanism has been elucidated.

Reactions with CNC_6H_{11} also differ from reactions with $CNCHMe_2$ in the nature of the Co(II) starting material: $[Co(CNC_6H_{11})_5](ClO_4)_2$ is prepared and immediately reacted in solution without first being isolated as $[Co_2(CNR)_{10}](ClO_4)_4 \cdot nH_2O$. Actually it has not been possible to isolate a stable sample of the dimeric complex; a maroon solid is observed at low temperature, but softens into blue tar upon filtration. Other alkylisocyanide–Co(II) complexes are isolated as maroon-red, diamagnetic solids, $[Co_2(CNR)_{10}]X_4 \cdot nH_2O$, $X = ClO_4$, BF_4; $R = CHMe_2$, CH_2Ph, $C_4H_9\text{-n}$ [5]; giving dark blue, paramagnetic solutions, presumably $[Co(CNR)_5]^{2+}$, in assumed analogy to $[Co_2(CNMe)_{10}](ClO_4)_4$ [6] and $[Co_2(CNEt)_{10}](ClO_4)_4$ [7].

Structures of the complexes

Physical properties of $\nu(-N{\equiv}C)$, solution electronic spectra, magnetic susceptibilities and molar conductivities are compatible with structures anticipated for these complexes. The $\nu(-N{\equiv}C)$ for $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ (Fig. 1) suggest a distorted trigonal bipyramidal structure in both solution and the solid state. IR and Raman solution spectra have been interpreted [8] as indicating a C_{2v} equatorially-distorted, axially-disubstituted trigonal bipyramidal structure for numerous $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes with arylisocyanide ligands. These IR spectra are analogous, although the solution patterns are poorly resolved. The $\nu(-N{\equiv}C)$ for $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ (Fig. 2) suggest tetragonal geometry, i.e. *trans*-$[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$. The shoulder in mull spectra suggests distortion of the CoC_4 plane, while the single strong band in solution is compatible with rigorous D_{4h} symmetry. Electronic spectra for $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ are similar to $[Co(CNR)_3(PR_3)_2]ClO_4$ spectra with $CNCHMe_2$ [1] and $CNCMe_3$ [9]. These were interpreted as charge-transfer bands. The single UV band for $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ appears to be charge-transfer in nature, but is strikingly narrow and symmetrical (see Fig. 3). Both complexes are diamagnetic, compatible with five-coordinate d^8 and six-coordinate d^6 configurations with strong field ligands.

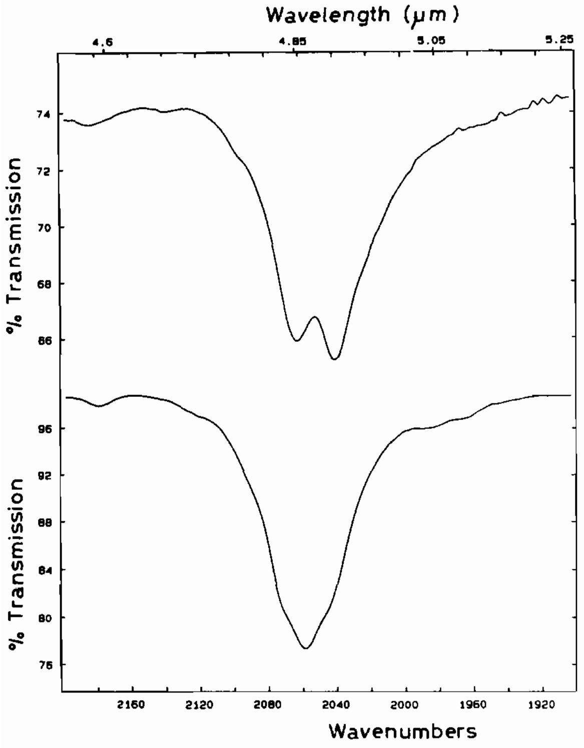

Fig. 1. The $\nu(-N{\equiv}C)$ pattern for $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$; nujol (top), CH_3NO_2 (bottom).

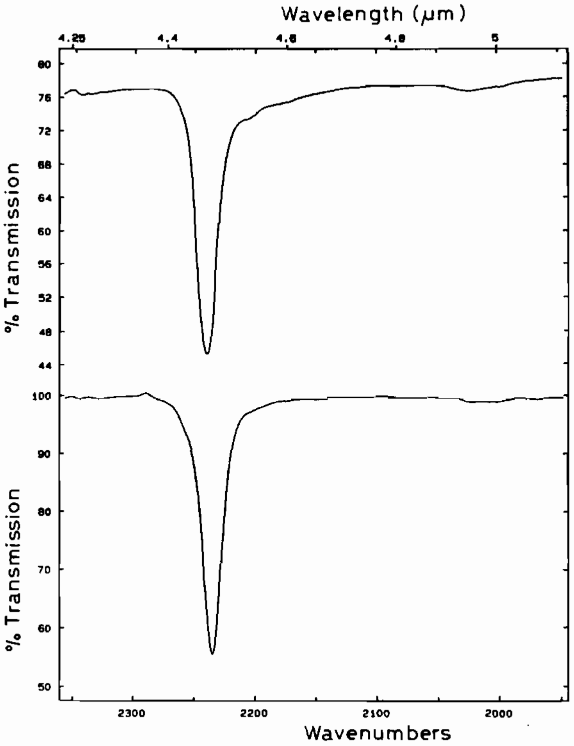

Fig. 2. The $\nu(-N{\equiv}C)$ pattern for $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$; nujol (top), CH_3NO_2 (bottom).

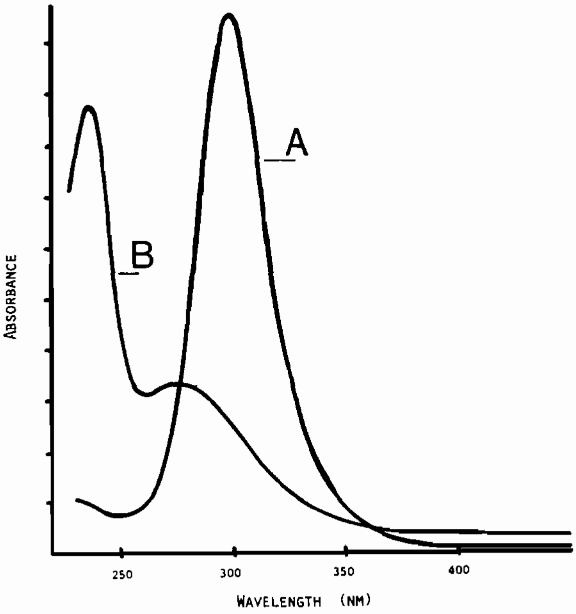

Fig. 3. The electronic spectra for $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-n})_3\}_2](ClO_4)_3$ (A) and $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ (B).

Molar conductivities for $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ in CH_3CN, $CH_3C(O)CH_3$, CH_3NO_2 and Me_2NCHO are appropriate for fully-dissociated 1:1 electrolytes [10], so values in CH_2Cl_2 and CF_3CH_2OH probably also reflect 1:1 electrolyte behavior. Conductivity values for $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$ are progressively low for 3:1 electrolytes in parallel with decreasing dielectric constants (ϵ). The Λ_M are marginally appropriate for fully-dissociated 3:1 electrolytes in CH_3CN and CH_3NO_2, but exhibit increasingly diminished values, indicative of increasing ion-pairing, for Me_2NCHO, CF_3CH_2OH, acetone and CH_2Cl_2. This is reasonable behavior for highly charged ions in organic solvents.

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