Inorganica Chimica Acta, 27 (1978) L105–L107
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Magnetic Moments for Pentakis(aromatic isocyanide)-cobalt(II) Complexes

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Received January 26, 1978

Pentakis(aromatic isocyanide)cobalt(II) perchlorates, $[Co(CNR)_5](ClO_4)_2$, R = C_6H_5, $C_6H_4CH_3$-2, $C_6H_4CH_3$-4, were initially prepared and characterized by Malatesta and Sacco [1]; later re-investigated by Pratt and Silverman [2], $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot 1.5H_2O$. Subsequent investigation [3] has established multiple forms of $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot xH_2O$ and $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot nS$ (S = solvent, n = 0.5, 1.0). This present work was initiated to study electronic spectra and magnetism for $[Co(CNR)_5]X_2$ (X = ClO_4, BF_4) with substituted arylisocyanides having different electronegativity and/or steric requirements.

Experimental

Magnetic susceptibilities were measured at room temperature (22–25 °C) by the Gouy-method using a five-place Mettler electrobalance, an Alpha Scientifics 7500 power supply, and an electromagnet operated at 5.0, 4.0, and 3.0 kG field strength. Pyrex Gouy tubes were calibrated [4] with $Hg[Co(SCN)_4]$ prepared from $CoSO_4 \cdot 7H_2O$ [5]. Infrared spectra were taken in nujol on a Beckman IR-7. Substituted N-phenylformamides were prepared from the corresponding anilines and formic acid [6]. Arylisocyanides were prepared from the appropriate phenylformamide by the method of Appel, Kleinstück, and Ziehn [7]. The isocyanides studied are summarized in Table I. Because of limited thermal stability (arylisocyanides polymerize upon heating) the isocyanides were vacuum (~0.1 torr) distilled or sublimed at minimum temperatures. Whether a particular isocyanide distills or sublimes is determined by its molecular weight and melting point. Isocyanides liquid at room temperature were reacted the same day as preparation since polymerization takes place upon attempted storage, but crystalline arylisocyanides can be stored under refrigeration indefinitely without apparent decomposition. The $4\text{-}CH_3OC_6H_4NC$ showed tendency for violet thermal decomposition under vacuum distillation. *CAUTION: Arylisocyanides are quite toxic and must be handled carefully, especially since one easily becomes de-sensitized to their vile odors. Inhaling amyl nitrite is the recommended antidote [8].*

The $[Co(CNR)_5]X_2 \cdot xH_2O$ (X = ClO_4, BF_4) complexes were prepared as previously described [9]: arylisocyanide in ethanol (29.1 mmol/45 ml) was added dropwise to a filtered, well-stirred solution of $Co(ClO_4)_2 \cdot 6H_2O$ or $Co(BF_4)_2 \cdot 6H_2O$ in ethanol (5.85 mmol/37 ml). To minimize reduction to Co(I), both solutions were maintained at 0 °C and the precipitate was immediately filtered and dried under suction/air. The crude product was washed with ethanol at 0 °C, filtered, and dried under suction/air. Yield of

TABLE I. Some Aromatic Isocyanides.

Isocyanide	Description of Product	Method (temp, °C) of Collection [a]	Melting Point (°C)[b]	ν(CN) (cm^{-1})
CNC_6H_5	Colorless liquid	Distills (19–22°)		2133
$CNC_6H_4CH_3$-4	Colorless liquid	Distills (28–30°)		2125
$CNC_6H_4CH_3$-2	Colorless liquid	Distills (31–41°)		2122
CNC_6H_4F-4	Yellow-green liquid	Distills (28–30°)		2142
CNC_6H_4Cl-4	Colorless crystals	Sublimes (80–90°)	71–73°	2127
CNC_6H_4Br-4	Colorless crystals	Sublimes (80–90°)	98–99°	2127
CNC_6H_4I-4	Colorless crystals	Sublimes (100–120°)	130–131°	2127
$CNC_6H_4C_2H_5$-2	Colorless liquid	Distills (40–42°)		2124
$CNC_6H_3(CH_3)_2$-2,6	Colorless crystals	Sublimes (45–55°)	74–75°	2121
$CNC_6H_3(C_2H_5)_2$-2,6	Colorless liquid	Distills (62–64°)		2119
$CNC_6H_2(CH_3)_3$-2,4,6	Colorless liquid	Distills (80–90°)	36–37°	2118
$CNC_6H_4OCH_3$-4	Colorless liquid	Distills (60–65°)		2135
$CNC_6H_4N(CH_3)_2$-4	Purple liquid	Distills (103–106°)		2122
$CNC_6H_4NO_2$-4	Colorless crystals	Sublimes (90–110°)	119–120°	2116

[a] Under vacuum (~0.1 torr). [b] Melting point (uncorrected) decomposition.

TABLE II. Arylisocyanide Complexes of Cobalt(II).

Complex	μ_{eff}[a] (B.M.)	Color[b]	IR (cm^{-1})[c] −N≡C	Analysis, Found[d] (Calcd)			
				%C	%H	%N	%Cl
$[Co(CNC_6H_5)_5](ClO_4)_2 \cdot 1.0H_2O$	2.08	lt. bl.	2222 s 2195 m	52.66 (53.12)	3.48 (3.44)	8.83 (8.85)	9.23 (8.96)
$[Co(CNC_6H_5)_5](BF_4)_2 \cdot 1.0H_2O$	2.03	v. lt. bl.	2219 s 2200 w	53.53 (53.61)	3.70 (3.73)	9.05 (8.93)	
$[Co(CNC_6H_4F\text{-}4)_5](ClO_4)_2$	2.26	lt. yel.	2252 vw* 2227 s	48.45 (48.67)	2.41 (2.33)	8.04 (8.11)	8.11 (8.21)
$[Co(CNC_6H_4CH_3\text{-}4)_5](ClO_4)_2$	2.33	lt. gr.	2246 w 2216 s 2196 m	56.76 (56.95)	4.22 (4.18)	8.30 (8.30)	8.43 (8.41)
$[Co(CNC_6H_4CH_3\text{-}4)_5](BF_4)_2 \cdot 1.0H_2O$	2.30	bl. gr.	2245 vw* 2215 s 2200 m	57.23 (57.45)	4.51 (4.46)		
$[Co(CNC_6H_4CH_3\text{-}2)_5](ClO_4)_2$	2.20	gr.	2235 vw* 2202 s	56.79 (56.95)	4.01 (4.18)	8.16 (8.30)	8.45 (8.41)
$[Co(CNC_6H_4CH_3\text{-}2)_5](BF_4)_2 \cdot 1.0H_2O$	2.39 2.46 2.71	dk. bl.	2235 vw* 2204 s 2187 s	57.19 (57.45)	4.52 (4.46)		
$[Co(CNC_6H_4C_2H_5\text{-}2)_5](ClO_4)_2$	2.30 2.38 2.47	gr.	2242 w 2210 s 2183 m	58.79 (59.15)	4.58 (4.96)	7.49 (7.66)	7.60 (7.76)
$[Co(CNC_6H_4C_2H_5\text{-}2)_5](BF_4)_2$	1.96	dk. gr. (m)	2245 w 2213 m 2191 s	61.00 (60.84)	5.17 (5.11)		
$[Co(CNC_6H_3\{CH_3\}_2\text{-}2,6)_5](ClO_4)_2 \cdot 0.5H_2O$	2.49 2.66 2.80	lt. gr. (m)	2235 w* 2213 s 2201 m	58.70 (58.58)	4.88 (5.03)	7.58 (7.59)	7.58 (7.68)
$[Co(CNC_6H_3\{CH_3\}_2\text{-}2,6)_5](BF_4)_2 \cdot 0.5H_2O$	2.17 2.38 2.44	lt. bl. (m)	2235 w* 2212 s	60.27 (60.23)	5.15 (5.17)		
$[Co(CNC_6H_3\{C_2H_5\}_2\text{-}2,6)_5](BF_4)_2 \cdot 1.0H_2O$	2.20	dk. bl. (m)	2206 s 2160 m 2120 w	63.07 (63.11)	6.45 (6.45)		
$[Co(CNC_6H_2\{CH_3\}_3\text{-}2,4,6)_5](ClO_4)_2$	2.46 2.54 2.73	bl. gr.	2240 vw* 2220 m* 2209 s 2193 m	60.93 (61.04)	5.45 (5.63)	7.06 (7.12)	6.87 (7.21)
$[Co(CNC_6H_2\{CH_3\}_3\text{-}2,4,6)_5](BF_4)_2$	2.77 2.95 3.18	gr.	2243 w 2212 s	62.35 (62.65)	5.72 (5.78)		

[a] For field-dependent moments, measurements at 5.0, 4.0, 3.0 kG, respectively. [b] v = very, lt = light, bl = blue, dk = dark, yel = yellow, gr = green, (m) = metallic luster. [c] vw = very weak, w = weak, m = medium, s = strong, * = unresolved. [d] Elemental analysis by Galbraith Laboratories, Knoxville, Tenn.

cobalt(II) complex was generally 85–90% except in cases of unusually high solubility such as $[Co(CNC_6H_3\{C_2H_5\}_2\text{-}2,6)_5](BF_4)_2 \cdot H_2O$. (The $[Co(CNC_6H_3\{C_2H_5\}_2\text{-}2,6)_5](ClO_4)_2$ was obtained in only trace amount due to extreme solubility in ethanol.) Chemically-pure $[Co(CNC_6H_4F\text{-}4)_5](ClO_4)_2$ was prepared, but reaction of $4\text{-}ClC_6H_4NC$, $4\text{-}Br_6H_4NC$, or $4\text{-}IC_6H_4NC$ with $Co(ClO_4)_2 \cdot 6H_2O$ (and $4\text{-}XC_6H_4NC$, X = F, Cl, Br, I) with $Co(BF_4)_2 \cdot 6H_2O$ resulted in physical mixtures of $[Co(CNC_6H_4X\text{-}4)_5](ClO_4)_2 \cdot xH_2O$ and $[Co(CNC_6H_4X\text{-}4)_5]ClO_4$ (evidenced by distinctly characteristic −N≡C ir) which were not separable by washing technique.

Results and Discussion

The arylisocyanide-cobalt(II) complexes prepared are summarized in Table II. Effective magnetic moments were calculated from measured susceptibilities according to standard procedure [4] $\mu_{eff} = 2.84 \sqrt{\chi'_M \cdot T}$ B.M. where $\chi'_M = \chi_g \cdot MW$ + diamagnetic correction. Tetrafluoroborate salts show greater tendency to adduct water and require longer dehydration times under strong vacuum than the corresponding perchlorate. While color is often not diagnostic, in this series blue complexes are hydrated, but green and especially yellow color suggests anhydrous nature. Hydrates that have been de-hydrated under vacuum (several hours to one week depending on complex) tend to be yellow powders. The –N≡C ir in general seems to be compatible with square pyramidal coordination, for which three ir-active fundamental –N≡C stretches are allowed but only a single band is often observed experimentally. Square pyramidal coordination has been suggested for $[Co(CNC_6H_5)_5](ClO_4)_2$ [2]. For mull spectra, however, C_{4v} or C_{2v} coordination of the isocyanides could not expect to be distinguished.

Complexes of phenyl- and *para*-substituted phenylisocyanides are clearly low-spin, their μ_{eff} range of 1.91–2.33 B.M. being reasonable for one unpaired electron ($\mu_{so} = 1.73$ B.M.). Theoretical crystal field calculations [10] suggest a $^2A_1[(b_2)^2(e)^4(a_1)]$ C_{4v} low-spin ground state for d′ Co(II), and $N_2(1)$-temperature mull electronic spectra have been satisfactorily fit [11] with $[Co(CNR)_5](ClO_4, BF_4)_2$, $R = C_6H_5$, $C_6H_4CH_3$-4, C_6H_4F-4, for this presumed ground state. Complexes of *ortho*-substituted pehnylisocyanides show magnetic moments often field-dependent and high for low-spin ground state. Their electronic spectra are analogous to those for the *para*-substituted phenylisocyanides but more complex and thereby not resolved by a C_{4v} treatment – such as expected if the symmetry were lowered to C_{2v}. Because of physical similarities throughout this analogous series, it is suggested that all complexes are low-spin but increases in μ_{eff} result through distortion from idealized square pyramidal coordination for sterically hindered arylisocyanides. Under C_{4v} the $^4E[(b_2)^2(e)^3(a_1)(b_1)]$ displaces $^2A_1[(b_2)^2(e)^4(a_1)]$ as ground state for estimated axial–basal bond angle greater than 110° [10], so under reduced symmetry it is not unreasonable to postulate a high-spin excited state sufficiently close to the low-spin ground state as to have significant room-temperature population.

Acknowledgment

Credit is due to Charles Glen Johnson (M.S., University of Texas at Austin, May 1973) who prepared most of these complexes.

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