Cobalt(III) Complexes with Cyanide and the Tetraamines 1,9-diamino-3,7-diazanonane and 1,10-Diamino-4,7-diazadecane [1]

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The reaction of trans-*(dichloro)(1,9-diamino-3,7-diazanonane)cobalt(III) chloride and* trans-*(dichloro)-(1,10-diamino-4,7-diazadecane)cobalt(III) chloride with sodium cyanide in aqueous solution is found to yield products with either* trans *or uns-*cis *stereochemistry depending on the reaction conditions. The stereochemistry of the products was determined by proton and carbon-13 NMR, electronic and vibrational spectroscopy. This is the first case where uns-*cis *diacido complexes with cobalt(III) and the tetraamines 1,9-diamino-3,7-diazanonane and 1,10-diamino-4,7-diazadecane have been prepared directly. Previous preparations of uns-*cis *complexes with these tetraamines have required an uns-*cis *complex with a chelating ligand as an intermediate. The stability of the uns-*cis *complexes is attributed to a greater degree of π bonding in the uns-*cis *complex compared with the corresponding* trans *complex. The difference in π bond energy must be greater than the 6 Kcal mol^{-1} difference in strain energy estimated from a molecular mechanics calculation.*

Introduction

In the chemistry of cobalt(III) complexes with tetradentate ligands, there are three possible topologies (Fig. 1) [2]. Normally, a single isomer is formed preferentially, consistent with classical mechanical strain energy estimates [3]. The consequences of intramolecular strain are seen in the preference of the *trans* isomer for cobalt(III) complexes with tetraamine and unidentate ligands and the uns-*cis* isomer for cobalt(III) complexes with tetraamine and chelating ligands. The only exceptions are the extensively studied complexes of 1,8-diamino-3,6-diazaoctane (TRIEN or 2,2,2-tet) where the strain energy of three coplanar five membered chelate rings in the *trans* complex is high enough to favor the other isomers [4]. Synthetic approaches to *cis*-diacido(polyamine)cobalt(III) complexes with ligands longer than 2,2,2-tet require the preparation of an uns-*cis* complex in one or more intermediates through the use of a chelating ligand [5]. The single exception is the synthesis of uns-*cis*-(dicyano)(1,10-diamino-4,7-diazadecane)cobalt(III) chloride [6] from *trans*-(dichloro)(1,10-diamino-4,7-diazadecane)cobalt(III) chloride.

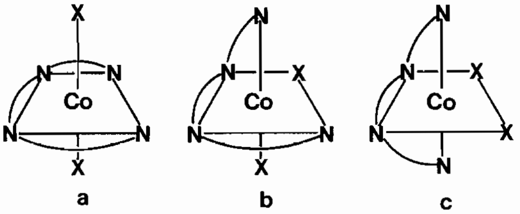

Fig. 1. Geometrical isomerism of six coordinate complexes with flexible tetradentate ligands. a) *trans*; b) uns-*cis*; c) s-*cis*.

In an attempt to characterize factors other than intramolecular strain which determine stereoisomerism in transition metal complexes, we have examined the effect of axial ligand field strength on ^{13}C NMR [7]. We found that 'crystal field' effects, though observable, are negligible compared with our estimates of intramolecular strain energy.

In the present work, we have undertaken the synthesis and characterization of both uns-*cis* and *trans* complexes of cobalt(III) and the flexible tetraamine ligands 1,9-diamino-3,7-diazanonane and 1,10-diamino-4,7-diazadecane. In this unique set of complexes, which do not conform to the predictions of classical strain energy minimization calculations, we seek evidence for additional electronic control of stereochemistry.

Experimental

Physical Methods

Elemental analysis

Analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario Canada.

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Electronic spectra

Electronic spectra were measured with a Cary Model 14 spectrophotometer. Samples were typically 1×10^{-3} *M* complex in aqueous solution.

Vibrational spectra

Vibrational spectra were measured with a Pye-Unicam model SP-300 spectrophotometer. Samples were prepared as nujol mulls between chloride windows and as potassium bromide pellets.

Proton magnetic resonance

High field proton NMR spectra were measured at 300 mHz using a Nicolet NT-300 NMR spectrometer. Samples were dissolved in a minimum amount of dimethylsulfoxide d_6 (99.9 atom% D, Aldrich). Tetramethylsilane was the internal reference for proton NMR measurements.

Carbon-13 nuclear magnetic resonance

Carbon-13 NMR measurements were made at 20 mHz with a Varian CFT-20 NMR spectrometer in the deuterium locked, proton noise decoupled mode. Samples were dissolved in a minimum amount of DMSO d_6 and placed in 10 mm NMR tubes (Wilmad). A pulse width of 21 microseconds (equivalent to a 90° pulse), a spectral width of 4000 Hz covered by 8192 data points and an acquisition time of 1.023 seconds was used for all complexes. Spectra were collected until an acceptable signal to noise ratio was achieved (10000–30000 spectra). All chemical shifts are reported relative to tetramethylsilane which was the internal reference for this study.

Ion exchange chromatography

A Sephadex C-25 ion exchange resin in the acid form was used for all ion exchange experiments.

Molecular mechanics calculations

Strain energy minimization calculations were performed on a PRIME 400 computer (32 bit internal precision) using a locally modified version of Boyd's MOLBD program [8]. A RMS coordinate shift of 1 pm with all non-bonded interactions within 300 pm included were accepted as convergence criteria. In cases where the initial coordinates were far from the minimized coordinates, a sinousoidal damping factor was placed on the coordinate shifts to prevent oscillation. All interaction constants have been published elsewhere [9]. A locally modified version of ORTEP [10] was used to produce the structure drawings.

Synthetic Methods

Trans-(dicyano)(1,9-diamino-3,7-diazanonane)cobalt(III) tetraphenylborate (*trans*-[Co(2,3,2-tet)(CN)$_2$]B(C$_6$H$_5$)$_4$, was prepared by the addition of 0.30 g (0.006 mol) of NaCN in 25 ml H$_2$O to a solution of 1.0 g (0.003 mol) *trans*-(dichloro)(1,9-diamino-3,7-diazanonane)cobalt(III) chloride (*trans*-[Co(2,3,2-tet)Cl$_2$]Cl) in 50 ml H$_2$O. The solution changed immediately from green to yellow-orange. The product was precipitated by the addition of a saturated aqueous solution of sodium tetraphenylborate, and recrystallized from hot acetone.

Uns-*cis*-(dicyano)(1,9-diamino-3,7-diazanonane)cobalt(III) chloride (uns-*cis*-[Co(2,3,2-tet)(CN)$_2$]Cl), was prepared by the addition of 1.0 g (0.003 mol) of *trans*-[Co(2,3,2-tet)Cl$_2$]Cl to a solution of 0.30 g NaCN in 50 ml H$_2$O. The resulting yellow solution was evaporated to dryness and the product collected. The product was recrystallized from ethanol/water (1:1/V:V).

Anal.: Calc. for $CoC_9H_{20}N_6Cl$: C, 35.2; H, 6.5; N, 27.3. Found: C, 34.8; H, 6.4; N, 26.9.

Trans-(dicyano)(1,10-diamino-4,7-diazadecane)cobalt(III) tetraphenylborate (*trans*-[Co(3,2,3-tet)(CN)$_2$]B(C$_6$H$_5$)$_4$), was prepared by the addition of 0.30 g (0.006 mol) of NaCN in 25 ml H$_2$O to a solution of 1.0 g (0.003 mol) *trans*-(dichloro)(1,10-diamino-4,7-diazanonane)cobalt(III) chloride (*trans*-[Co(3,2,3-tet)Cl$_2$]Cl) in 50 ml H$_2$O. The solution changed immediately from green to yellow-orange. The product was precipitated by the addition of a saturated aqueous solution of sodium tetraphenylborate, and recrystallized from hot acetone.

Uns-*cis*-(dicyano)(1,10-diamino-4,7-diazadecane)-cobalt(III) chloride (uns-*cis*[Co(3,2,3-tet)(CN)$_2$]Cl), was prepared by the addition of 1.0 g (0.003 mol) of *trans*-[Co(3,2,3-tet)Cl$_2$]Cl to a solution of 0.30 g NaCN in 50 ml H$_2$O. The resulting yellow solution was evaporated to dryness and the product collected. The product was recrystallized from ethanol/water (1:1/V:V).

Anal.: Calc. for $CoC_{10}H_{22}N_6Cl$: C, 37.3; H, 6.8; N, 26.1 Found: C, 37.0; H, 6.8; N, 26.0.

Results

Synthesis

The reaction of *trans*-[Co(2,3,2-tet)Cl$_2$]Cl and *trans*-[Co(3,2,3-tet)Cl$_2$]Cl with sodium cyanide in water at 80 °C is found to produce uns-*cis*-[Co(2,3,2-tet)(CN)$_2$]Cl and uns-*cis*-[Co(3,2,3-tet)(CN)$_2$]Cl respectively. The reaction of cyanide with either of the *trans* dichloro complexes is extremely rapid, with the yellow-orange color of the dicyano complex appearing within the time of mixing. After isolation of the product by reducing the volume and recrystallization from ethanol:water (1:1/V:V), the complex had completely isomerized to the uns-*cis* complex. These conditions, above ambient temperature and long reaction times, usually produce the *trans* isomer exclusively. Ion exchange chromatography of an aqueous solution of the obtained solid on Sephadex

C-25 ion exchange resin using 0.1 *M* $NaClO_4$ eluant showed no NMR evidence of the *trans* complex.

Syntheses were also attempted at lower temperatures in dimethylsulfoxide, conditions previously used for the preparation of *trans* dicyano complexes with other polyamines [11]. Immediate ion exchange chromatography of the resulting solution under the conditions described above initially showed about 25% of the more mobile *trans* isomer. Attempts to isolate a product from this fraction were not successful.

Preparation of the *trans* isomer of these complexes depends on the rapid substitution of cyanide for chloride and the slow isomerization rates for cobalt(III) tetraamine complexes [12]. Addition of sodium cyanide to an aqueous solution of the *trans* dichloro complex, followed by the addition of a saturated aqueous solution of sodium tetraphenylborate produced an immediate precipitate of the *trans* complex which always contained an excess of the tetraphenyl borate salt. About 10% (weight) of the product is sodium tetraphenylborate which can not be separated by recrystallization because of the ready isomerization of the desired product. Attempted synthesis of the *trans* complexes using other anions to precipitate the product yielded only a small amount of insoluble brown product.

Nuclear Magnetic Resonance

The proton NMR spectra of all of the cyano complexes in DMSO D_6 show the same features as other cobalt complexes with the same tetraamine ligands and stereochemistry [13]. The proton NMR of the *trans* isomers do, however, show an excess of the tetraphenylborate anion.

The carbon-13 NMR spectra of the complexes is the most conclusive proof of their stereochemistry, since the uns-*cis* isomer has lower symmetry than the *trans* and s-*cis* isomers. The *trans* isomer is distinguished from the s-*cis* isomer on the basis of the large chemical shift differences between these isomers observed in the corresponding TRIEN complexes. While the s-*cis* isomer has never been observed in complexes with 2,3,2-tet or 3,2,3-tet [2], the chemical shifts are expected to differ substantially from those of the well known *trans* isomers. Moreover, the observed ^{13}C NMR of *trans* dicyano complexes shows the same features as the other known *trans* complexes.

The uns-*cis* isomer, because of its low symmetry is expected to show a larger number of resonances than the *trans* isomer [14]. The observed spectrum cannot easily distinguish between the uns-*cis* isomer and an equimolar mixture of the *trans* and s-*cis* isomers, but greater chemical shift differences would be expected from the s-*cis* isomer. In addition to the high strain of the s-*cis* isomer, the formation of a 50–50 mixture of the *trans* and s-*cis* isomers in complexes with both tetraamine ligands would be unlikely.

Vibrational and Electronic Spectroscopy

The vibrational spectra of all complexes, run as Nujol mulls between salt plates, shows evidence of coordinated cyanide and the tetraamine ligand (CN stretching frequencies of 2,160 cm^{-1} for *trans*-$[Co(2,3,2\text{-tet})(CN)_2]^+$, 2,145 cm^{-1} for uns-*cis*-$[Co(2,3,2\text{-tet})(CN)_2]^+$, 2,165 cm^{-1} for *trans*-$[Co(3,2,3\text{-tet})(CN)_2]^+$ and 2,145 cm^{-1} uns-*cis*-$[Co(3,2,3\text{-tet})(CN)_2]^+$). The possibility of coordinated water in any of these complexes is precluded by the absence of an O–H stretch in the 3,000–3,400 cm^{-1} region of infrared spectrum [15].

The electronic spectra of the uns-*cis* isomers exhibits two well resolved bands in the near ultraviolet (320 nm, 31.3 kK; 410 nm, 24.4 kK). The low energy band shows a shoulder on the low energy side (445 nm, 22.5 kK) due to splitting of the octahedral $^1T_{1g}$ state into two components under the approximately tetragonal symmetry [16, 17] of the complexes. In common with other related complexes, the higher energy band shows no splitting [17].

The electronic spectra of the two *trans* complexes is dominated by an intense band in the near ultraviolet, assigned to a metal ligand charge transfer transition. A shoulder on the low energy side of this band (390 nm, 25.6 kK) may be one of the expected d–d transitions. The absence of bands in the visible region of the spectrum precludes the presence of substantial concentrations of either the *trans* dichloro complexes or aquation products.

Molecular Mechanics

A molecular mechanics study of the strain energies of both the dichloro and dicyano complexes of cobalt(III) and the tetraamines 2,3,2-tet and 3,2,3-tet was undertaken in an attempt to determine the role of classically calculated intramolecular strain in the observed stability of the uns-*cis* isomer. A comparison of the calculated strain energies shows no significant energy differences between the dichloro and dicyano complexes. The structures calculated for *trans*-$[Co(2,3,2\text{-tet})(CN)_2]^+$, *trans*-$[Co(3,2,3\text{-tet})(CN)_2]^+$ and uns-*cis*-$[Co(3,2,3\text{-tet})(CN)_2]^+$ are similar to the crystal structures observed for complexes with the same stereochemistry and tetraamine ligand [18–20]. The calculated structure of uns-*cis*-$[Co(2,3,2\text{-tet})(CN)_2]^+$ has chelate ring conformations consistent with circular dichroism and NMR spectra [21].

The calculated energies for the various complexes are shown in Table I. The energy difference between the *trans* isomer and the related uns-*cis* isomer is sufficiently large that none of the uns-*cis* isomer should be prepared under equilibrium conditions (4–7 kcal mol^{-1}). These strain energies are consistent with the observations on most of the other diacido complexes [9].

TABLE I. Strain Energy Minimization Results for Some Dichloro- and Dicyano(tetraamine)cobalt(III) Complexes.

Complex	R_{ij}[a]	θ_{ijk}	ϕ_{ijkl}	NB_{ij}	Total
trans[Co(2,3,2-tet)Cl_2]$^+$	2.04	3.86	1.39	5.15	12.44
trans[Co(2,3,2-tet)$(CN)_2$]$^+$	2.15	3.74	1.43	4.83	12.15
uns-*cis*[Co(2,3,2-tet)Cl_2]$^+$	2.31	6.25	4.17	6.96	19.96
uns-*cis*[Co(2,3,2-tet)$(CN)_2$]$^+$	2.28	6.03	4.23	6.46	19.00
trans[Co(3,2,3-tet)Cl_2]$^+$	2.61	6.56	0.89	7.59	17.67
trans[Co(3,2,3-tet)$(CN)_2$]$^+$	2.32	6.36	0.89	6.73	16.30
uns-*cis*[Co(3,2,3-tet)Cl_2]$^+$	3.07	8.44	0.59	9.15	21.25
uns-*cis*[Co(3,2,3-tet)$(CN)_2$]$^+$	2.97	8.38	0.57	8.86	20.78

[a] Energies in kcal mol^{-1}.

Discussion

The synthesis of the uns-*cis* isomer under conditions which normally yield the *trans* isomer suggests some basic difference between cyanide and other ligands whose complexes are known. Contributions from classically calculated intramolecular strain energy are identical in the dicyano and *trans* dominated diacido complexes, and predict the stabilization of the *trans* isomer by some 6 kcal mol^{-1}. Contributions from crystal field effects are probably negligible, since in complexes with other, more sterically demanding polydentate ligands, the isomeric distribution in the cyano complexes is comparable with all other unidentate mixed ligand complexes. Moreover, the observed relative stabilities of the *trans* and uns-*cis* isomers of the spectrochemically similar nitrite ion are as expected.

The most reasonable explanation for the apparent stability of uns-*cis* dicyano complexes lies in the ability of cyanide, serving as a 'π acid', to engage in π bonding with the filled orbitals of the metal ion. There are four potentially π acceptor orbitals on the two cyanide ligands, and three available π symmetry orbitals on the central ion. In the trivial symmetry of the *cis* complex, all orbitals transform as A; in the C_2 symmetry of the *trans* complex, the central ion π orbitals transform as A + 2B and the cyanide π orbitals transform as 2A + 2B. Clearly, in either isomer three fourths of the π^* orbitals may participate in bonding with the central ion. Using the simple pictorial 'orbital extension' model of Ballhausen and Gray [22], however, it is evident that in the *trans* complex the π^* orbitals of the cyanide ions compete for the central ions of B symmetry (d_{xz} and d_{yz}), with the A orbital involved to a lesser extent. In the *cis* complex, the dominant bonding pattern should involve independent interaction of the cyanide ions with the d_{xy} and d_{xz} or d_{yz} orbitals of the central ion, and hence a stronger bonding interaction, all else being equal.

Evidence supporting greater π bonding in the complexes with uns-*cis* geometry arises from the vibrational and ^{13}C NMR spectra of the complexes. The presence of π bonding involving the cyanide ligands requires the participation of cyanide π^* orbitals, the population of which decreases the strength of the C–N bond. The decreased strength of the C–N in the uns-*cis* complex is reflected in the 15–20 cm^{-1} decrease in the vibration frequency of the uns-*cis* complex when compared with the *trans* complex [15].

Previously, the effects of changes in the electronic distribution at the cobalt ion on the ^{13}C NMR spectrum of the ligand were detailed. The effects were interpreted in terms of a simple electron repulsion argument in which electrons in the filled symmetry orbitals of the cobalt ion are forced away from the axial ligands and toward the tetraamine ligand, thereby increasing the shielding, as the axial field strength increased. The ^{13}C NMR of the appropriate carbon atoms of the *trans* dicyano complexes indicates an attraction of these electrons toward cyanide as evidenced by the higher than expected chemical shift (*i.e.*, deshielding) of the carbon atoms of the five membered chelate ring. This attraction of the electrons is expected if a π bonding molecular orbital is formed between the metal filled orbitals and the π^* antibonding orbitals of the cyanide ion.

Conclusions

The evidence presented above suggests an explanation of the unexpected stereochemistries observed for the cyanide complexes of cobalt(III) and the tetraamines 3,2,3-tet and 2,3,2-tet. The π bonding in complexes with cyanide may be the principal reason for the unexplained stereochemistry of the thermodynamically favored complex. The slow isomerization reactions of cobalt(III) complexes with the ligands 2,3,2-tet and 3,2,3-tet allow the *trans* isomer to be prepared under kinetic control. Finally, the first complexes where the uns-*cis* isomer is favored over the *trans* isomer, in cobalt(III) complexes with the tetraamine ligands 2,3,2-tet and

3,2,3-tet and unidentate ligands have been prepared and characterized using proton NMR, ^{13}C NMR and infrared spectroscopy. Clearly, in complexes with strong bonding ligands (presumably π donors as well as π acceptors), classical molecular mechanics calculations cannot predict molecular structure.

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