Inorganica Chimica Acta, 64 (1982) L99–L100
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Linkage Isomerism in Cyanoaquobis(dimethylglyoximato)cobalt(III)

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Received August 3, 1981

Cyanide ions readily coordinate to transition metals forming metal–carbon bonds, while N-bonding ability is less favoured (due to the greater electronegativity of the nitrogen atom and the consequent lower availability of the electron pair localized in a nitrogen σ-antibonding orbital [1, 2]). Consequently, isocyano complexes are rarely isolated.

Employing $[Ag(CN)_2]^-$ as a source of cyano groups, we have been able to isolate the isocyano compound $[Co(NC)(H_2O)(dmgH)_2]$, isostructural with the previously described cyano compound $[Co(CN)(H_2O)(dmgH)_2]$ (where $dmgH_2$ = dimethylglyoxime) [3].

Experimental

Products

$[Co(NC)(H_2O)(dmgH)_2]$

2.0 g of $[Co(NH_3)_2(dmgH)_2]Cl\cdot 5H_2O$ [4] dissolved in 30 ml of water were mixed with a solution of 0.96 g of $K[Ag(CN)_2]$ in 30 ml of water. The resulting solution yields a precipitate of $[Co(NH_3)_2(dmgH)_2][Ag(CN)_2]$; the resulting suspension is refluxed for five minutes after complete redissolution of the precipitate and then allowed to cool overnight. The yellow-orange product is separated with a yield of 25%.

$[Co(CN)(H_2O)(dmgH)_2]$

In addition to the usual synthesis [3], this product can be obtained by heating the isocyano complex in an oven at 250–260 °C for an hour.

Analysis

Cobalt was determined by EDTA titrimetry after mineralisation. Cyanide was distilled as hydrogen cyanide over a solution of sodium carbonate and then titrated with silver. Organic nitrogen was determined by Kjeldahl's method.

Spectral Measurements

X-Ray diffraction spectra and structure adjustment were been carried out at the Departamento de Cristalografía of this University [5].

IR spectra in the range 2000–2500 cm^{-1} were obtained from KBr disks on a Beckman IR-20A spectrophotometer calibrated against a polystyrene film, with an accuracy of ± 2 cm^{-1}.

Raman spectra in the same range were obtained from the solid in capillary tubes on a Dilor spectrophotometer equipped with a triple monochromator at the Laboratoire de Chimie Minerale D, Université des Sciences et Techniques du Languedoc (Montpellier), using as exciting light the 5145 Å line of an argon laser, the accuracy being ±2 cm^{-1}.

Results and Discussion

Both complexes are isostructural (see Fig. 1), having the usual planar arrangement of the bis(dimethylglyoximato) moiety, the cyano isomer being best formulated as $[Co(CN)(H_2O)(dmgH_2)(dmgH)]$ as found frequently for bis(dimethylglyoximato)-cobalt(III) derivatives [6, 7]. Some selected interatomic distances are shown in Table I. For the C-cyano complexes, the carbon–nitrogen bond distance of the cyano group is slightly shorter while its Co–O bond distance is slightly longer.

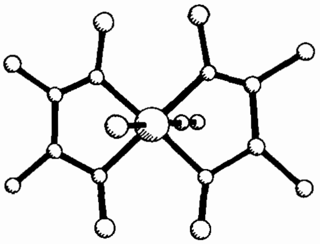

Fig. 1. Molecular structure for both isomers (hydrogen atoms not shown).

TABLE I. Selected Bond Distances (Å). A: $[Co(CN)(H_2O)(dmgH)_2]$; B: $[Co(NC)(H_2O)(dmgH)_2]$.

Co–N (dmgH)	1.89	1.89 (mean value)
Co–O (H_2O)	1.992(4)	1.984(3)
Co–C	1.906(5)	–
Co–N (NC)	–	1.903(4)
C≡N	1.141(7)	1.149(6)

Infrared and Raman spectra show a single band in the CN stretching region (see Table II) for each compound. The lesser σ-antibonding donor ability of the

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TABLE II. Properties and Analytical Data, Found % (Calcd. %). Wavelengths in cm^{-1}.

Compound	Colour	Effect of Heat or Laser	ν(CN)	Co	CN^-	Organic N
$[Co(CN)(H_2O)(dmgH)_2]$	brown	none	2186	17.52 (17.69)	7.70 (7.80)	16.77 (16.81)
$[Co(NC)(H_2O)(dmgH)_2]$	orange	changes to brown	2136	17.58	7.64	16.97

isocyano group gives rise to a lower CN bond order, responsible for the lower CN stretching frequency as well as for the differences in CN bond distances. A further consequence of the greater σ-donation of the C-cyano is an increase in the electron density of the cobalt atom axial orbitals (mainly d_{z^2}), thus weakening the Co–O axial bond. It is noteworthy, however, that the CN stretching frequency is far more sensitive to the bonding differences than is the CN bond distance.

The difference in colour between the complexes is explained by the lower position of the -NC ligand in the spectrochemical series [8].

When recording the Raman spectrum of the isocyano derivative, the band at 2136 cm^{-1} quickly disappears while a strong band becomes evident at 2186 cm^{-1}. This fact can be attributed either to a photochemical isomerization reaction upon laser irradiation, or to the thermal process promoted by local heating by the laser beam:

$$[Co(NC)(H_2O)(dmgH)_2] \xrightarrow[\text{or } \Delta]{h\nu} [Co(CN)(H_2O)(dmgH)_2]$$

in agreement with the greater stability expected for the C-bonded isomer.

The formation of the N-bonded complex takes place in the reaction of $[Co(NH_3)_2(dmgH)_2]^+$ with $[Ag(CN)_2]^-$, while the C-bonded complex is formed upon reaction of the same cation with the cyanide ion. These facts suggest the existence of a bridged intermediate species which may undergo cleavage of the Ag–C bond, thus leaving the isocyano–cobalt group (the pH of the solution, approximately 10, facilitates the hydrolysis of the NH_3 ligands).

Some authors have previously reported similar isomerization reactions with [9–11] or without [12–14] the intervention of Ag^+ or Hg^{2+} ions, but the products obtained are either binuclear compounds (with the cyano group acting as a bridge) or isocyano intermediates, which are not isolated. Several cyano bridged compounds containing the $Co(dmgH)_2^+$ skeleton have been described [15–20], but they are not known to produce complexes with a monodentate isocyano ligand.

Current work is being done to test the validity of the reported reaction as a useful synthetic route to isocyano cobalt complexes.

Acknowledgements

The authors are indebted to Dr. B. Bonnet for recording the Raman spectra and to Dr. X. Solans for helpful discussions on the molecular structures.

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