Metal Stabilized Cyanoisocyanide; X-Ray Structure of [Cr(CO)₅CNCN]

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 $[Cr(CO)_5CNCN]_3$ and $[Cr(CO)_5CNCN]$ are synthesized by action on NEt₄ $[Cr(CN)(CO)_5]$ of cyanuric chloride and cyanogen chloride, respectively; the molecular structure of pentacarbonyl(cyanoisocyanide)-chromium(0) is established by single crystal X-ray diffraction.

The nonexisting isomers of NCCN (cyanogen), viz. CNNC and CNCN have repeatedly attracted interest since the days of W. A. Hofmann.¹ Of the various procedures devised for their synthesis, however, none was successful. The recent generation and stabilization in metal complexes of a number of unusual isocyanides such as CNH,² CNNH₂,³ and CNCCl₃,⁴ suggested a similar route to obtain the CNCN molecule.

Reaction in dichloromethane of NEt₄[Cr(CN)(CO)₅]⁵ with cyanuric chloride (3:1, room temperature, 18 h) followed by evaporation and recrystallization gave (63% yield) orange crystals of μ_3 -2,4,6-tri-isocyanotriazine-tris(pentacarbonylchromium) (1) [i.r. (CH₂Cl₂): 2116w, 2047w, 1975vs, 1952sh, 1481s, 1330m cm⁻¹, m.s. (70 eV): M^+ and characteristic fragmentation]. Heating of the trimer to the decomposition point (140—145 °C) and above did not result in the formation of detectable amounts of the monomer (2).

Monomeric pentacarbonyl(cyanoisocyanide)chromium (2) can be conveniently prepared, however, by bubbling ClCN through a cold solution of NEt₄[Cr(CN)(CO)₅] (0 °C, 5 min), and is purified by sublimation to give moderate yields (23 %) of colourless, plate-like crystals {i.r. (cyclohexane): 2246m, 2102w, 2019m, 1992s, 1952s(br) cm⁻¹, m.s. (70 eV): M^+ (peak intensity *ca.* 20%), [Cr(CO)_nCNCN]⁺ (n = 1—4), [Cr-CNCN]⁺ (66%), [CrCN]⁺ (100%)}. *Crystal data:* C₇CrN₂O₅, M = 244.08, monoclinic, space

Crystal data: $C_7 \text{CrN}_2 O_5$, M = 244.08, monoclinic, space group $P2_1/c$, Z = 4, a = 13.010(2), b = 6.373(3), c = 11.790(1) Å, $\beta = 98.13(1)^\circ$, R = 0.042 ($R_w = 0.044$) for 1559 reflections (Philips PW 1100 four-circle diffractometer, monochromatised Ag- K_{α} X-radiation).[†]



The molecular structure of (2) is shown in Figure 1. With an angle at the isocyanide N atom of $168.5(4)^\circ$, the CNCN moiety deviates considerably from linearity. Slightly yet significantly different CN triple bond lengths are displayed by the isocyanide[‡] and cyanide groups being separated by an extremely short NC single bond. A similar though less drastic shortening of a formal NC single bond [1.354(5) Å] has been found in (OC)₅CrC=N-C=Co₃(CO)₉ (3) and taken as evidence of the acetylenic character of the methylidyne C atom.⁶

No parallel can be drawn, however, between the respective dimensions in the $Cr(CO)_5$ fragments of (2) and (3). Thus, while in (3) a comparatively short $Cr-C(O)_{trans}$ meets with a relatively long $C-O_{trans}$ distance reflecting the weak *trans*-influence of a typical *C*-isocyanide, the opposite, *i.e.* an elongated Cr-C(3) along with a shortened C(3)-O(3), is true of (2). Together with the short Cr-C(2) bond of 1.883(3) Å [as against 1.961(4) Å in (3)] this points to a particularly strong metal isocyanide interaction. That in fact we are dealing with an isocyanide of unusual ligand properties is

[†] The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

 $[\]ddagger$ A CrNCCN sequence can be ruled out on the basis of the less favourable R values and thermal parameters obtained for this mode of linkage.



Figure 1. The structure (ORTEP, 40% probability) of $[Cr(CO)_5-CNCN]$ with atomic numbering scheme and important molecular parameters. Averaged bond lengths are given for the *cis* Cr–C and C–O groups.

further borne out by the $v_{NC,CO,CN}$ i.r. pattern§ and a strikingly low isocyano ¹³C resonance {[²H₈]tetrahydrofuran, δ 212.6 (CO), 200.0 (CrCN), 125.7 (NCN) p.p.m.} as well as

¹³C-Labelling in (2) of the isocyano-carbon causes the 1952 cm⁻¹ band only (!) to shift to lower wavenumbers.

by recent calculations showing CNCN to be a much better π -acceptor than CO.⁷

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