

Organometallic Octahedro-octahedra: Hexakis(penta-carbonyl(cyano)chromato-N)silicate, -germanate, and -stannate[†]

E. BÄR, W. P. FEHLHAMMER*

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabockstrasse 34-36, D-1000 Berlin 33, F.R.G.

D. K. BREITINGER and J. MINK**

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-8520 Erlangen, F.R.G.

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The addition of electrophiles to cyano complexes not only afforded the very first isocyanides [1] but

[†]Dedicated to Prof. Dr. Dr. h.c. mult. E. O. Fischer on the occasion of his 65th birthday.

*Author to whom correspondence should be addressed.

**Permanent address: Institute of Isotopes, Hungarian Academy of Sciences, 1525 Budapest, Hungary.

also represents a synthetic method of continuing interest. Besides alkyl, haloalkyl [2], and acyl [3] isocyanides and isocyanide complexes, a series of boranyl [4], silyl to plumbyl [5], phosphoranyl, and sulfonyl [6] isocyanides have recently been prepared in which the Group III to VI elements are linked directly to the isocyano nitrogen. With the exception of the diisocyanides $[B(NC)_2X_2]^-$ (X = F, B) [7] and $B(NC)_2(OMe) \cdot NMe_3$ [4], which act as bridges between two metal atoms, all of the heteroelement isocyanides are *monoisocyanides*.

Here we report on *hexaisocyanides* or *hexaisocyanide* complexes of silicon, germanium and tin which are stabilized by coordination to six $Cr(CO)_5$ fragments.

Action of $NEt_4[Cr(CN)(CO)_5]$ on $SiCl_4$ in a 4:1 molar ratio surprisingly gave $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ as the only identifiable product. When the reaction was repeated using a 6:1 stoichiometry, as required by eqn. 1, the yield improved considerably:

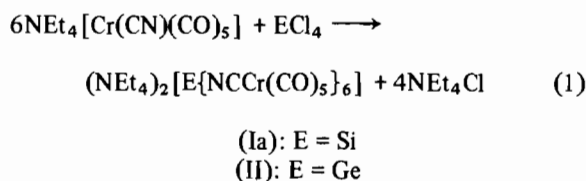


TABLE I. IR^a and Raman^{b,c} Solution Spectra (cm^{-1}) of Compounds I–III in the NC and CO Stretching Frequency Region.

Compound	$\nu(NC)$		$\nu(CO)$	
	IR	Ra	IR	Ra
Ia	2132m-s	2166s,P	2051s	2050vs
		2131m,DP	1994sh	1989s
Ib	2107m-s	2125s,P	1956vs	1918w,b
		2103m,DP	1921vs,b	
II	2122m-s	2125s,P	2039s	2037s-vs
		2121m-s,DP	1988sh	1990s
III	2114m-s,b	2149s,P	1955vs	1962vw
		2102sh,DP	1920vs,b	1919w,b
III	2114m-s,b	2149s,P	2052s	2046s
		2102sh,DP	1990sh	1988s
III	2114m-s,b	2119s,b,P	1951vs	1918w,b
		2102sh,DP	1922sh	
III	2114m-s,b	2119s,b,P	2047s	2042s
		2102sh,DP	1988sh	1988s
III	2114m-s,b	2119s,b,P	1951vs	1923w,b
		2102sh,DP	1925s,sh	

^aZeiss IMR 16 spectrometer, CH_2Cl_2 solution. ^bCary 82 spectrometer, Spectra Physics 164 Kr⁺ ion laser ($\lambda = 647.1$ nm), CH_3OH solution. ^cP = polarized, DP = depolarized.

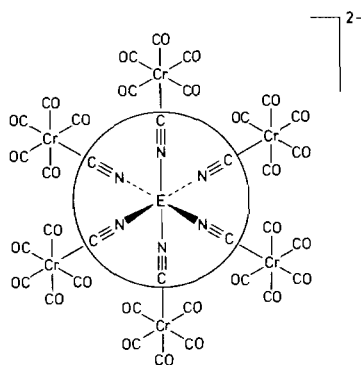


Fig. 1. Suggested structure of the heptanuclear anions of I–III.

The germanium analogue II and the ^{13}C -labelled compound $(\text{NEt}_4)_2[\text{Si}\{\text{N}^{13}\text{CCr}(\text{CO})_5\}_6]$ (Ib) could be obtained following the same procedure. For the synthesis of $(\text{NEt}_4)_2[\text{Sn}\{\text{NCCr}(\text{CO})_5\}_6]$ (III), however, hexachlorostannate was used as a starting material. The pale yellow to yellow complexes are soluble in polar solvents such as acetone or methanol, in which they show the expected conductivities [cf. 8]. There is no indication of solvolysis nor of hydrolysis, even if these solvents contain minor amounts of water. According to conductivity measurements only partial dissociation (resp. ion pair formation) occurs in dichloromethane, which is by no means uncommon in this solvent [8].

Compounds I–III are fully characterized by their elemental analyses and vibrational spectra (Table I). Additional information is provided by ^{13}C -NMR data of Ia and Ib. The chemical shift of the isocyano carbon ($\delta(^{13}\text{C}) = 166.3$ ppm, solvent $\text{CO}(\text{CD}_3)_2$) downfield from that of $[\text{Cr}(\text{CN})(\text{CO})_5]^-$ (146.8 ppm) clearly reflects the bonding of an electrophile to the nitrogen end of the cyano complex, and is in accordance with those of the more common C-isocyanide complexes [9].

The structure of the heptanuclear anions (Fig. 1) is suggested mainly on the basis of infrared and Raman studies. On labelling the isocyano group in Ib with ^{13}C , characteristic isotope shifts are observed which allow unequivocal assignment of the $\nu(\text{NC})$ vibrations. Compared with $[\text{Cr}(\text{CN})(\text{CO})_5]^-$, the $\nu(\text{NC})$ frequencies in Ia–III have moved to higher values (the same is true for the pair of ^{13}C labelled compounds), indicating the bridging function of the CN groups. The presence of only one $\nu(\text{NC})$ band (T_{1u}) in the IR, and of one totally polarized (A_{1g}) and one depolarized band (E_g) in the Raman spectrum, together with the observed mutual exclusion rule, are highly indicative of an octahedral array of the NC groups about E.

In case of an overall O_h symmetry, three IR (T_{1u}) and six Raman active CO stretching vibrations ($2A_{1g} + 3E_g + T_{2g}$) are calculated; for local C_{4v} symmetry of the $\text{Cr}(\text{CO})_5$ fragments, three IR ($2A_1 + E$) and four Raman bands ($2A_1 + B_2 + E$) are to be expected. Obviously, the actual spectra are governed by the selection rules of local C_{4v} symmetry to a first approximation. A more detailed discussion of the complete vibrational spectra will be given elsewhere [10].

Studies on analogous systems with central transition metal atoms are in progress.

Experimental

Tetraethylammonium-hexakis{pentacarbonyl(cyano)-chromato-N}silicate, $(\text{NEt}_4)_2[\text{Si}\{\text{NCCr}(\text{CO})_5\}_6]$ (Ia)

SiCl_4 (0.057 ml, 0.50 mmol) was added to a filtered solution of $\text{NEt}_4[\text{Cr}(\text{CN})(\text{CO})_5]$ (1.044 g, 3.00 mmol) in 40 ml CH_2Cl_2 . The mixture was stirred for 24 h at room temperature. The creamy-white precipitate was collected, washed with four 5 ml- portions of cold dichloromethane, and dried under vacuum. A second crop of Ia was obtained by adding n-hexane to the washings and storing at -20°C . The total yield of Ia was 0.48 g (60%). *Anal.* Calc. for $\text{C}_{52}\text{H}_{40}\text{Cr}_6\text{N}_8\text{O}_{30}\text{Si}$: C, 39.10; H, 2.51; N, 7.02; Cr, 19.55; Si, 1.76%. Found: C, 39.23; H, 2.60; N, 7.06; Cr, 19.20; Si, 1.96%. The molar conductivity Λ_M (22°C , acetone) was $251 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at $3.0 \times 10^{-5} \text{ M}$. Crystalline Ia is stable indefinitely at room temperature but decomposes above 147°C .

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