Acta Chemica Scandinavica A 32 (1978) 47 – 50

The Crystal Structure of Hexakis(phenyl isocyanide)chromium(0), $Cr(CNC_6H_5)_6$

EVERT LJUNGSTRÖM

Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology, P.O.Box, S-402 20 Göteborg 5, Sweden

The crystal structure of hexakis(phenyl isocyanide)-chromium(0), $Cr(CNC_6H_5)_6$ has been determined by single crystal X-ray methods. The compound crystallizes in space group $R\bar{3}$ with $a = 10.574(7)$ Å and $\alpha = 111.41(5)°$, $Z = 1$. A final R value of 0.044 was obtained for 1030 independent reflexions. The isocyanide groups have an almost octahedral arrangement around the chromium atom with Cr – C and C – N bond lengths of 1.938(3) and 1.176(4) Å, respectively. The Cr – C – N angle is 173.7(2)° and the C – N – C angle is 172.9(3)°.

The nature of the metal-ligand bond in transition metal isocyanide complexes has been the subject of much interest in recent years. Evidence for considerable π-bonding, especially in complexes with a formally zerovalent metal atom has come from spectroscopical studies [1,2] and a few X-ray structure determinations.[3-6] Some semi-empirical molecular orbital calculations have also been performed, the results of which are in good agreement with available experimental data.[4,7,8] The X-ray studies and the MO calculations have dealt mainly with alkylisocyanide complexes.

Strong similarities can be expected between transition metal hexaisocyanide complexes and the corresponding hexacyanide complexes. In connection with an investigation on bonding in transition metal hexacyanides, in progress at this department, M(II) – C(N) bond distances have been found to be shorter than their M(III) – C(N) counterparts, indicating an increase in the π-contribution to the M – C bond with decreasing formal oxidation state of the metal ion. Crystal structure studies on transition metal hexaisocyanide complexes have now been started in order to extend the investigation to metal ions with a low formal charge.

EXPERIMENTAL

The compound was prepared by the method due to Malatesta *et al.*, in which an alcoholic suspension of chromium(II) acetate is treated with an excess of phenyl isocyanide.[9] Phenyl isocyanide was prepared according to Malatesta and purified by vacuum distillation immediately before use.[10] Red rhombohedric crystals suitable for X-ray work were obtained from a benzene solution of the compound into which light petroleum vapor (b.p. 60 – 80 °C) was allowed to diffuse.

A crystal of dimensions 0.11 × 0.18 × 0.19 mm was chosen for the data collection. Intensities were collected for $\sin\theta/\lambda \leq 0.76$ with a SYNTEX $P2_1$ automatic four-circle diffractometer using graphite monochromatized Mo radiation. The $\omega - 2\theta$ scan method was used and the 2θ scan speed was allowed to vary between 2 and 10° min^{-1}, depending on the intensity of the measured reflexion. Preliminary investigations showed the thermal motion of the atoms to be considerable and the crystal was therefore cooled to −105 °C using the SYNTEX LT 1 low temperature device. Cell parameters were determined from a least squares fit of the refined diffractometer setting angles for 15 reflexions.

No separate measurements of background were made during data collection. A profile analysis based on the Larsen-Lehmann method was instead applied to the 96 step profile collected for each reflexion.[11] Correction was made for Lorentz and polarization effects and from the 2130 measured independent reflexions 1030 with $F_o^2 \geq 3\sigma(F_o^2)$ were considered as being observed and were used in the subsequent calculations.

CRYSTAL DATA

Hexakis(phenyl isocyanide)chromium, $Cr(CNC_6H_5)_6$; M = 670.7 trigonal, space group $R\bar{3}$

with $a = 10.574(7)$ Å and $\alpha = 111.41(5)°$ at -105 °C [$a = 10.658(7)$ Å and $\alpha = 111.22(5)°$ at 22 °C] $U = 838.5$ Å^3. $Z = 1$, $D_x = 1.328$ g cm^{-1}, $D_m = 1.33$ g cm^{-1}, μ(Mo) = 3.0 cm^{-1}. The compound crystallizes as bright red rhombohedric crystals.

STRUCTURE DETERMINATION

The positions of all the non-hydrogen atoms were found from a Patterson map and subsequent electron density calculations (DRF).[12] Refinement of an overall scale factor, atomic coordinates and anisotropic thermal parameters, using the block diagonal approximation, converged at an R-value of 0.065 (BLOCK)[12] ($R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$). Due to the chromium atom being on a site of symmetry $\bar{3}$ its thermal parameters U_{22}, U_{33}, U_{13} and U_{23} were not included in the refinement but after each cycle the shift on U_{11} was applied to U_{22} and U_{33} and the shift on U_{12} was applied to U_{13} and U_{23}. A difference synthesis calculated with the parameters obtained in the block refinement revealed the hydrogen atoms as the five highest peaks in the map (DRF).[12] Introducing these atoms with isotropic thermal motion and using full matrix least squares refinement an R-value of 0.044 was obtained for the 95 parameters (LALS).[12] The weighting scheme used was that of Cruickshank [$w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$] with $a = 12.0$, $c = 0.04$ and $d = 0$.[13] The atomic scattering factors for Cr(0), C and N were those due to Doyle and Turner[14] while those for H were taken from Stewart, Davidson and Simpson.[15] A final difference synthesis showed no peaks higher than 0.35 e Å^{-3}.

RESULTS AND DISCUSSION

The final atomic coordinates and thermal parameters are given in Tables 1 and 2, respectively. Distances and angles within the molecule are listed in Table 3. The values in Table 3 are calculated using the low temperature cell parameters. Fig. 1 shows a stereoscopic projection of part of the structure (ORTEP).[12] The chromium atom is approximately octahedrally coordinated by the six isocyanide ligands, the deviation from the ideal 90° C–Cr–C angle being 4.1°. A plane defined by the phenyl groups of one centrosymmetrically related pair of ligands approximately contains the isocyanide C and N atoms of one of the two remaining pairs while the CN groups of the last pair are nearly perpendicular to this plane (Fig. 1). The maximum deviation from a least squares plane through the ring carbon atoms is 0.006 Å for the ring carbon atoms and 0.04 Å for the hydrogen atoms. The molecules pack with the planes of neighbouring phenyl groups practically parallel. The shortest C–C distance between two such rings is 3.13 Å.

Table 1. Atomic coordinates with their standard deviations. C(2)–C(7) belong to the phenyl ring. The hydrogen atoms are numbered according to the carbon atom to which they are bonded.

Atom	x/a	y/a	z/a
Cr	0	0	0
C(1)	0.0797(3)	0.2263(3)	0.0709(3)
N(1)	0.1400(3)	0.3683(3)	0.1277(3)
C(2)	0.1913(3)	0.5304(3)	0.1841(3)
C(3)	0.1892(3)	0.5809(3)	0.0786(3)
C(4)	0.2328(3)	0.7401(3)	0.1313(4)
C(5)	0.2787(3)	0.8494(3)	0.2880(4)
C(6)	0.2828(4)	0.7997(4)	0.3937(4)
C(7)	0.2382(4)	0.6402(4)	0.3421(4)
H(3)	0.505(4)	−0.031(4)	0.161(4)
H(4)	0.773(4)	0.061(4)	0.227(4)
H(5)	0.955(5)	0.321(5)	0.308(5)
H(6)	0.877(5)	0.498(5)	0.312(5)
H(7)	0.615(5)	0.418(5)	0.246(5)

Table 2. Thermal parameters ($\times 10^3$ for the non hydrogen atoms) and their standard deviations. The anisotropic temperature factor has the form $\exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + a^*b^*hkU_{12} + a^*c^*hlU_{13} + b^*c^*klU_{23})]$. The isotropic temperature factor is $\exp\{-B[(\sin\theta)/\lambda]^2\}$.

Atom	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	20.9(4)	20.9	20.9	29(1)	29	29
C(1)	27(1)	28(1)	27(1)	35(2)	33(2)	38(2)
N(1)	35(1)	27(1)	46(1)	35(2)	41(2)	46(2)
C(2)	22(1)	22(1)	34(1)	22(2)	29(2)	33(2)
C(3)	29(1)	29(1)	30(1)	32(2)	38(2)	33(2)
C(4)	27(1)	29(1)	37(1)	29(2)	39(2)	45(2)
C(5)	34(1)	24(1)	42(1)	32(2)	45(2)	34(2)
C(6)	44(2)	34(2)	33(2)	41(3)	46(3)	31(3)
C(7)	34(1)	34(1)	30(1)	33(3)	32(2)	40(3)
H(3)	1.1(7)					
H(4)	0.7(6)					
H(5)	2.0(8)					
H(6)	2.2(8)					
H(7)	2.0(8)					

Table 3. Distances (Å) and angles (°) in $Cr(CNC_6H_5)_6$ at −105 °C with their standard deviations. The atoms C(2)−C(7) belong to the phenyl ring and the hydrogen atoms are numbered according to the carbon atom to which they are bonded.

Cr−C(1)	1.938(3)	C(4)−C(5)	1.386(5)
C(1)−N(1)	1.176(4)	C(5)−C(6)	1.392(4)
N(1)−C(2)	1.388(4)	C(6)−C(7)	1.387(4)
C(2)−C(3)	1.398(4)	C(7)−C(2)	1.394(4)
C(3)−C(4)	1.385(4)	C(3)−H(3)	0.99(3)
C(4)−H(4)	0.93(3)	C(5)−H(5)	0.93(4)
C(6)−H(6)	0.94(4)	C(7)−H(7)	0.92(4)
C(1)−Cr−C(1)′	85.9(2)	Cr−C(1)−N(1)	173.7(2)
C(1)−N(1)−C(2)	172.9(3)	N(1)−C(2)−C(3)	119.4(3)
N(1)−C(2)−C(7)	120.4(3)	C(3)−C(2)−C(7)	120.2(2)
C(4)−C(3)−C(2)	119.7(3)	C(5)−C(4)−C(3)	120.3(3)
C(6)−C(5)−C(4)	119.9(3)	C(7)−C(6)−C(5)	120.4(3)
C(2)−C(7)−C(6)	119.5(3)		

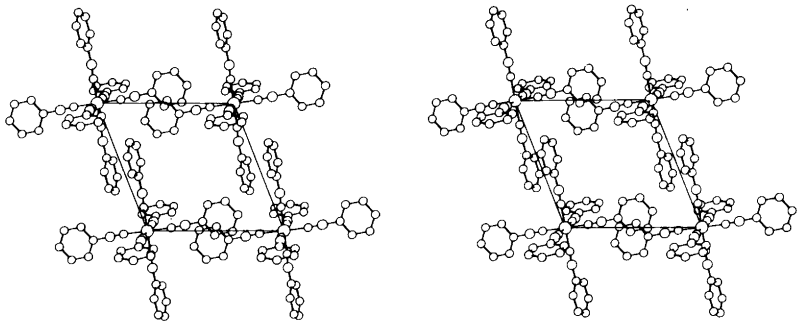

Fig. 1. Stereoscopic projection of $Cr(CNC_6H_5)_6$ perpendicular to the *ab* plane.

The metal-ligand bonding in the hexakis(phenyl isocyanide)chromium(0) molecule has been discussed in Refs. 1 and 2. The lowering of the infrared C−N stretch frequency from 2130 cm^{-1} in the free ligand to two peaks at 2012 and 1965 cm^{-1} in the complex has been interpreted in terms of a weakening of the C−N bond due to partial filling of the π^*_{C-N} orbitals. The short Cr(0)−C bond of 1.938(3) Å found in this investigation indeed indicates that extensive d-π^* back donation takes place. The Cr(0)−C bond is significantly shorter than the Cr(II)−C bond of 2.053(4) Å found in $Na_4[Cr(CN)_6].10H_2O$ [16] and the Cr(III)−C bond of 2.077(5) Å in $K_3[Cr(CN)_6]$.[17] The difference in formal charge on the central atom alone should have an effect opposite to that observed. The tendency in this series confirms the theory that a low formal charge on the metal atom enhances the π-contribution to the metal-ligand bond.

Although several hexaaryl isocyanide Cr(0) complexes have been prepared,[2,9] no hexaalkyl isocyanide Cr(0) complex is known. It would appear that the aromatic part of the ligand stabilizes the complex. The orientation of the rings relative to the rest of the molecule in the present compound is favourable for interaction between part of the C−N π system and the π system of the ring. Delocalization of the backdonated electrons over the whole ligand should make an aryl isocyanide ligand a better π-acceptor than an alkyl isocyanide. Such a delocalization ought, in principle, to be detectable in the C−C bond lengths of the benzene ring. The C−C bond lengths in hexakis(phenyl isocyanide)chromium(0) do not, however, deviate significantly from the normal phenyl C−C value.

Acknowledgements. The author wishes to thank Professor N.-G. Vannerberg for valuable discussions and Dr. S. Jagner for revising the English text. The work has been supported financially by the Swedish Natural Science Research Council (NFR 2286-026).

REFERENCES

1. Mann, K. R., Cimolino, M., Geoffroy, G. L., Hammond, G. S., Orio, A. A., Albertin, G. and Gray, H. B. *Inorg. Chim. Acta 16* (1976) 97.
2. Cotton, F. A. and Zingales, F. *J. Am. Chem. Soc. 83* (1961) 351.
3. Cotton, F. A., Dunne, T. G. and Wood, J. S. *Inorg. Chem. 4* (1965) 318.
4. Sarapu, A. C. and Fenske, R. F. *Inorg. Chem. 11* (1972) 3021.
5. Cotton, F. A., Dunne, T. G. and Wood, J. S. *Inorg. Chem. 3* (1964) 1495.
6. Joshi, K. K., Mills, O. S., Paulson, P. L., Shaw, B. W. and Stubbs, W. H. *Chem. Commun.* (1965) 181.
7. Sarapu, A. C. and Fenske, R. F. *Inorg. Chem. 14* (1975) 247.
8. Fantucci, P., Naldini, L., Cariati, F., Valenti, V. and Bussetto, C. *J. Organomet. Chem. 64* (1974) 109.
9. Malatesta, L., Sacco, A. and Ghielmi, S. *Gazz. Chim. Ital. 82* (1952) 516.
10. Malatesta, L. *Gazz. Chim. Ital. 77* (1947) 238.
11. Lehmann, M. S. and Larsen, F. K. *Acta Crystallog. A 30* (1974) 580.
12. Program library of Department of Inorganic Chemistry, University of Göteborg and Chalmers University of Technology: DRF written by Zalkin, A., BLOCK by Lindgren, O., LALS by Gantzel, P., Sparks, R. and Trueblood, T. and ORTEP by Johnson, C. K.
13. Cruickshank, D. W. J. In *Crystallographic Computing*, Munksgaard, Copenhagen 1970, p. 195.
14. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A 24* (1968) 390.
15. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
16. Ljungström, E. *Acta Chem. Scand. A 31* (1977) 104.
17. Jagner, S., Ljungström, E. and Vannerberg, N.-G. *Acta Chem. Scand. A 28* (1974) 623.

Received July 21, 1977.