Neutron Diffraction Study on a Single Crystal of Pentacarbonyldiethylcyanamidechromium at 110 K†

Marie-Noëlle Ohnet,[a] Anne Spasojević-de Biré,[a] Nguyen Quy Dao,*[,a] Peter Schweiss,[b,c] Markus Braden,[b] Helmut Fischer[d] and David Reindl[d]

[a] *Laboratoire de Physico-Chimie Moléculaire et Minérale, E.R.S. 0070 du C.N.R.S., Ecole Centrale Paris, F-92295 Châtenay - Malabry Cédex, France*
[b] *Laboratoire Léon Brillouin, unité mixte CEA-CNRS, CE Saclay, F-91191 Gif sur Yvette Cédex, France*
[c] *Fakultät für Chemie, Universität Konstanz, Postfach 5560, M727, D-78434 Konstanz, Germany*
[d] *Kernforschungszentrum Karlsruhe, INFP, Postfach 3640, D-76021 Karlsruhe, Germany*

The crystal structure of the complex [Cr(NCNEt$_2$)(CO)$_5$] has been determined by neutron diffraction at 110 K. The crystal used was twinned and the twin law was analysed. The structure is composed of layers of molecules parallel to the twin plane which are held together by van der Waals interactions and intermolecular hydrogen bonds. The cyanamide ligand has an intermediate σ-donor:π-acceptor ratio, stronger, for example, than the carbene ligand. There are two types of *cis*-carbonyl groups in the structure, resulting from the conjugation effect of the cyanamide skeleton in the molecule. Charge transfer, which is characteristic of the delocalization of the lone pair of the amino nitrogen along the six-atom linear chain, is observed along the bonds on the binary molecular axis, including the *trans*-carbonyl group.

During the last fifteen years, the chemistry of metallaheterocumulene organometallic complexes has made great progress and new families of compounds have been synthesized. We have been interested in the synthesis and physico-chemical properties of complexes of type [M(CO)$_5$L] where the ligands L form a linear arrangement with the metal of at least four heteroatoms. Three different families have been studied: neutral allenylidene complexes[1] of formula [M(=C=C=CR$_2$)(CO)$_5$] (M = Cr or W, R = Ph), 2-azaallenylidene complexes [M(=C=N=CR$_2$)(CO)$_5$] which are mostly obtained in the cationic form[2] (M = Cr or W, R = Bu^t) and which also crystallize in the radical form[3] (M = Cr or W, R = C$_6$H$_2$Me$_3$), and neutral aminonitrile or cyanamide complexes[4] [M(=N=C=NR$_2$)(CO)$_5$] (M = Cr or W, R = Et or Me). In these complexes the M(CO)$_5$ coordination entity is important as the substitution of the *trans* ligand by a halogen atom leads to a bent carbyne complex,[5] and by reductive dimerization, a dinuclear complex is obtained.[6] It has been shown that these compounds, which possess several multiple bonds, are good intermediate reagents for the synthesis of new complexes, and some of them are excellent organic catalysts.[7] In addition, the linear fragment can be described by a succession of three double bonds, the π-electron planes being perpendicular to each other. This geometry favours a strong delocalization and the bond order which is formally two can vary from one to three. The conjugation between different multiple bonds in allenylidene and 2-azaallenylidene comples[8,9] may be described by several mesomer forms in equations (1) and (2) respectively, where M = Cr, Mo or W, R = alkyl group.

$$(OC)_5M{=}C_\alpha{=}C_\beta{=}C_\gamma R_2 \longleftrightarrow (OC)_5\underset{-}{M}{-}C_\alpha{\equiv}C_\beta{-}\overset{+}{C}_\gamma R_2 \longleftrightarrow (OC)_5\overset{-}{M}{-}\overset{+}{C}_\alpha{=}C_\beta{=}C_\gamma R_2 \quad (1)$$

$$(OC)_5M{=}C_\alpha{=}\overset{+}{N}_\beta{=}C_\gamma R_2 \longleftrightarrow (OC)_5\overset{-}{M}{-}C_\alpha{\equiv}\overset{+}{N}_\beta{-}\overset{+}{C}_\gamma R_2 \quad (2)$$

As part of the studies on the nature of the chemical bonds in organometallic compounds using electron-deformation density[10] and vibrational spectrometry,[11] we are now concerned with charge transfer in metallaheterocumulene complexes. The pentacarbonyldiethylcyanamidechromium complex of formula [Cr(NCNEt$_2$)(CO)$_5$] **1** was chosen because it crystallizes in large single crystals which are suitable for a neutron-diffraction experiment. Here we present the neutron structure results of **1** at 110 K, as the first step of this project. Comparisons are made with similar complexes and also with the X-ray diffraction results reported previously by Fischer *et al.*[4] at 243 K.

Experimental

Synthesis of [Cr(NCNEt$_2$)(CO)$_5$].—The synthesis was carried out at low temperature (≈230 K) in an inert atmosphere, using anhydrous solvents saturated with nitrogen. A solution of hexacarbonyl-chromium (or -tungsten) (10 mmol) in tetrahydrofuran (thf) was irradiated with mercury light until no trace of the starting material could be detected by infrared spectroscopy, giving the intermediate product, [Cr(CO)$_5$·thf]. After the addition of diethylcyanamide (10 mmol) N≡C–NEt$_2$, the solution was shaken for 1 h and the solvent removed *in vacuo*. The product obtained was purified by chromatography on silica gel using a pentane–CH$_2$Cl$_2$ (1:1) mixture as eluent. Crystallization from pentane–CH$_2$Cl$_2$ (4:1) gave yellow crystals of **1**, which is very sensitive to oxygen and can only be handled and stored in an inert atmosphere.

Structure Determination.—Data collection. The single crystal used for the neutron-diffraction experiment was a pentagonal prism (40 mm^3). It was fixed inside an aluminium sheet with silicon grease in a dry cooled-helium jet. The sample was then glued on an aluminium pin inside a cylindrical aluminium box filled with helium and mounted on the goniometer of the diffractometer.

The neutron-diffraction data were collected using the 5C2 four-circle diffractometer (λ = 83.1 pm) of the Orphée

---

† Chemical Bonding in Metallaheterocumulene Complexes. Part 1.
Supplementary data available (No. SUP 57050, 28 pp.): anisotropic thermal parameters, observed and calculated intensities and a projection of the structure along the $\vec{c}$ axis for [Cr(NCNEt$_2$)(CO)$_5$]. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Reactor, Saclay, France. The crystal was maintained at 110(1) K with a closed-cycle helium refrigerator (Air Products and Chemical Inc., Displex model CS-202) during the 3 w experiment. The orientation matrix was determined from a set of 18 reflections and the parameters were refined: $a = 1340(3)$, $b = 1135(2)$, $c = 929.1(7)$ pm and $\beta = 116.08(12)°$, space group $C2/c$, the same observed by the X-ray diffraction experiment[4] at 243 K.

The intensity data were collected for one complete quadrant of the reciprocal sphere and about $\frac{2}{3}$ of a second quadrant. Intensities of two reflections ($\bar{1}\bar{2}$ 0 0) and (0 0 4), monitored after every 300 min, were constant within 3% and 1% respectively. The ω-scan method was used for intensity recording, and scanning widths were accorded to the instrumental resolution by the equation $(\Delta\omega)^2 = (16 - 54 \tan\theta + 88 \tan^2\theta)$. Lorentz and numerical absorption[12] corrections were applied. Because of the lack of precise values of the bonded hydrogen-atom mass-absorption coefficient, this value was obtained by a refinement procedure. The retained value $\mu = 1.2$ cm^{-1} gave the best internal reliability factor for all equivalent reflection sets. The minimum and maximum transmission coefficients were 0.63 and 0.72 respectively. 3703 Reflections were recorded with $(\sin\theta)/\lambda$ between 0.06 and 0.74 Å^{-1} (indices were in the range $h = \overline{19}$–17, k = 0–16 and l = 0–13), leading to 2173 independent reflections of which 1294 had $I \geqslant 3\sigma$ with an internal reliability factor $R_{\text{int}}(I) = 0.056$ $\{R_{\text{int}}(I) = \Sigma_{K=1}^{M} [\Sigma_{J=1}^{N}(I_M - I_J)^2]_K / \Sigma_K \Sigma_J (I_J^2)_K$ where I_M = averaged intensity, N = number of symmetrically equivalent reflections, M = number of symmetrically independent reflections J = the sum over a symmetric equivalent group and K = the sum over symmetric independent reflections$\}$.

Twinning. Two of the best crystals were tested for the neutron-diffraction experiment. Unfortunately, both of them were twinned; however, one showed that the twinning was quite simple and could be used for a precise measurement of diffracted intensities. It possessed two twin elements (I and II). The twin plane, determined by neutron diffraction, was the $\vec{b}$, $\vec{c}$ plane: all the reflections of type $hk0$ were superimposed and those of type hkl ($l \neq 0$) were well separated. There were 99 observed superimposed $(hk0)_{\text{I}}$ and $(hk0)_{\text{II}}$ reflections. To determine precisely the proportion of the two elements I and II, two methods were used after the determination and refinement of the orientation matrixes of I and II. The first method consisted of recording the intensity of five identical hkl reflections of I and II which were completely spatially resolved. The ratio ρ of the same reflections $[I(hkl)_{\text{I}}/I(hkl)_{\text{II}}]$ gives the proportion of the twins; here, $\rho = 0.22(1)$. The second procedure is an *a posteriori* calculation. During the refinement, a scale factor k_1 was used for the non-superimposed hkl ($l \neq 0$) reflections and a second scale factor k_2 for the 99 superimposed $(hk0)_{\text{I}} + (hk0)_{\text{II}}$ reflections. The observed intensity of the $hk0$ reflections can be expressed as: $I_{\text{obs}}(hk0) = I_{\text{obs}}(hk0)_{\text{I}} + \rho I_{\text{obs}}(hk0)_{\text{II}}$ where $\rho = (k_2 - k_1)/k_1$. The refinement gives $k_1 = 2.09(1)$ and $k_2 = 2.52(1)$ corresponding to $\rho = 0.21(1)$ in good agreement with the independent determination.

For data collection, only the hkl reflections corresponding to the first larger domain were recorded. However, 48 reflections were accidentally superimposed. Their indices for the second domain were identified and corrections were carried out and included in the final refinement using the refined value [0.21(1)].

Least-squares refinements. Full-matrix least-squares refinements were performed using the PROMETHEUS program package.[12] Coherent scattering lengths for Cr, C, N, O, H were taken from ref. 13, and an extinction correction, using the Becker–Coppens model[14] assuming a type-I crystal with Lorentzian mosaicity distribution was applied. Finally, the refinement converged* to $R(F^2) = 0.058$, $wR(F^2) = 0.050$ and goodness of fit $(S) = 5.54$ for 1273 reflections with $I > 3\sigma$ and 132 parameters (consisting of two scale factors, the isotropic extinction parameter, nuclear position and anisotropic thermal parameters). The extinction parameter g was found to be $0.062(2) \times 10^{-4}$. Only five reflections had an extinction correction greater than 10%.

Table 1 gives the atomic coordinates of compound **1** at 110 K. Despite the presence of the twins, the collection of the neutron-diffraction data is of a good quality as shown by the R values and the estimated standard deviations. The neutron results allow us to discuss for the first time the nature of the chemical bonds in this family of complexes.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Description of the Structure.—Fig. 1 shows the molecular structure of $[Cr(NCNEt_2)(CO)_5]$ and Fig. 2 shows the crystal arrangement projected along the $\vec{b}$ axis. The interatomic distances, bond angles and torsion angles are given in Table 2.

The results obtained by neutron diffraction confirm more precisely the structure determined previously by X-ray diffraction[4] at 243 K. The cyanamide group constitutes one of the six ligands co-ordinated to chromium possessing an almost planar skeleton. The small deviation from a perfect planar arrangement is caused by the C(4)–C(5) bonds of the ethyl groups which form a dihedral angle of 6.0(1)° with the C(β)N(γ)C(4) plane. The ligand has two N–C axial bonds of different lengths, N(α)–C(β) 116.7(2) and C(β)–N(γ) 130.4(2) pm, respectively, and two equivalent amino bonds, N(γ)–C(4) 147.2(1) pm, with a C–C distance of 151.1(2) pm in the ethyl group. The five C–H distances are almost equal with an average length of 109.3(4) pm. The six atoms O(1), C(1), Cr, N(α), C(β) and N(γ) form a linear chain on the binary axis. Regarding the carbonyl ligands, the *trans*-Cr–C(1) axial distance of 185.0(3) pm is shorter than the average Cr–C distance in the *cis*-carbonyl groups (191.4(1) pm). At the same time, a slightly longer distance for the axial carbonyl group [C(1)–O(1) 115.4(3) pm] is observed compared to the average length of *cis*-C≡O groups [114.0(3) pm]. The two *cis*-C(2)O(2) carbonyl groups are closest to the ethyl groups; C(2) lies 13.2 pm above the equatorial plane at the level of the Cr atom with N(γ)–Cr–O(2) 88.5(1)°, while the two C(3)O(3) groups are situated 9.5(1) pm below this plane [N(γ)–Cr–O(3) 94.3(1)]. The angles between the C(2)CrN(γ) plane and the two CrN(γ)C(4) and CrN(γ)C(5)

Table 1 Atomic positions of $[Cr(NCNEt_2)(CO)_5]$ at 110 K

Atom	x	y	z
Cr	0	0.1578(3)	0.25
C(1)	0	−0.0045(1)	0.25
O(1)	0	−0.1058(2)	0.25
N(α)	0	0.3388(1)	0.25
C(β)	0	0.4412(1)	0.25
N(γ)	0	0.5556(1)	0.25
C(2)	0.1096(1)	0.1620(1)	0.4679(1)
O(2)	0.1757(1)	0.1649(2)	0.5979(2)
C(3)	0.1151(1)	0.1499(1)	0.1821(1)
O(3)	0.1832(1)	0.1375(1)	0.1424(2)
C(4)	−0.0760(1)	0.6224(1)	0.1088(1)
C(5)	−0.1578(1)	0.5453(1)	−0.0217(1)
H(41)	−0.1187(3)	0.6861(3)	0.1502(4)
H(42)	−0.0256(3)	0.6732(3)	0.0649(4)
H(51)	−0.2088(3)	0.4958(3)	0.0206(4)
H(52)	−0.2132(3)	0.5995(3)	−0.1213(4)
H(53)	−0.1171(3)	0.4827(3)	−0.0677(4)

---

* $R(F^2) = \Sigma_H |F_o^2 - (k|F_c|)^2| / \Sigma_H F_o^2$, $wR(F^2) = \{\Sigma_H w|F_o^2 - (k|F_c|)^2|^2 / \Sigma_H wF_o^4\}^{\frac{1}{2}}$ and $S = \{\Sigma_H w(|F_o| - k|F_c|)^2/(N_o - N_v)\}^{\frac{1}{2}}$, where $w = 1/\sigma^2(F^2)$, H are the Miller indices, N_o = number of reflections and N_v = number of independent parameters ($N_o - N_v$ = number of degrees of freedom).

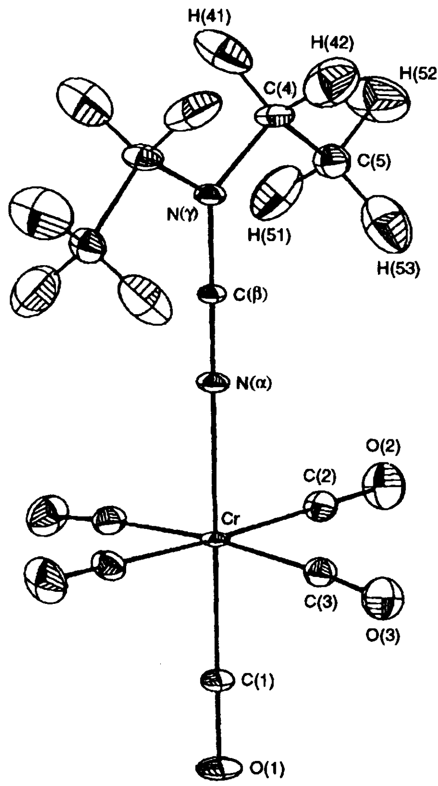

Fig. 1 Molecular structure[15] of [Cr(NCNEt$_2$)(CO)$_5$] at 110 K

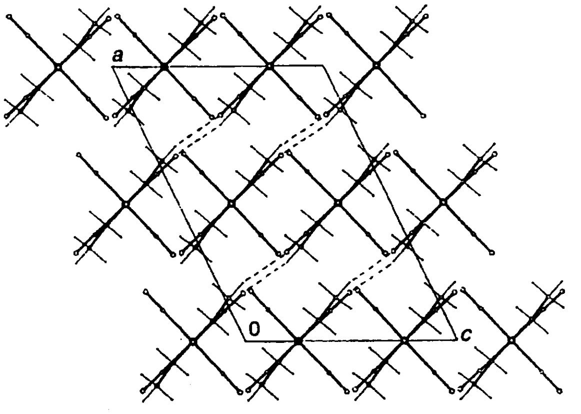

Fig. 2 Projection of the structure[16] of [Cr(NCNEt$_2$)(CO)$_5$] along the $\vec{b}$ axis

planes are 2.9(1) and 6.2(1)°, respectively. Hence, the two *cis*-C(2)O(2) carbonyl groups are in a nearly eclipsed position with respect to the ethyl group and they are moved closer to them. It should be noted that even though the C–H distances of the ethyl groups are practically equal the H(52) proton close to the C(2)CrN(γ) plane forms the shortest hydrogen bond to a neighbouring molecule [C(5)–H(52) $\cdots$ O(2$^{\mathrm{II}}$) 248.3 pm (Table 3)].

Comparison with the Crystal Structure determined by X-Ray Diffraction at 243 K.—The general features of compound **1** and its organization in the crystal are similar at 110 and 243 K.[4] Nevertheless, a careful comparison with the structure determined by X-ray diffraction (Table 2) shows some significant differences. For instance, the C–H distances determined by neutron diffraction are accurate and homogeneous. Also, for the atoms with strongly delocalized electronic clouds the neutron diffraction distances between them [*e.g.*, Cr–C(1), Cr–C(2), Cr–C(3)] are slightly longer than those from X-ray diffraction. This has also been observed for other metal carbonyl complexes, [Cr(≡CC$_6$H$_5$)Cl(CO)$_4$][17] and [K(C$_{18}$H$_{36}$N$_2$O$_6$)]$^+$-[Cr$_2$(μ-H)(CO)$_{10}$]$^-$ (C$_{18}$H$_{36}$N$_2$O$_6$ = 4,7,13,16,21,24-tetraoxa-1,10-diazabicyclo[8.8.8]hexacosane)[18] and for the free cyanamide ligand.[19,20]

trans-*Effect on the Carbonyl Group exerted by the Cyanamide Ligand.*—In [Cr(CO)$_6$], as studied by neutron diffraction[21] at 78 K, the average Cr–C and C≡O distances are respectively 191.8(1) and 114.1(1) pm and are thus very similar to the Cr–C$_{cis}$ and *cis*-C≡O distances in **1**. In contrast, the observed Cr–C$_{trans}$ bond distance in **1** [Cr–C(1) 185.0(3) pm] is shorter and the corresponding *trans*-C≡O distance [C(1)–O(1) 115.4(3) pm] is slightly longer than in [Cr(CO)$_6$], in agreement with the correlation of Cr–C and C≡O bond distances in chromium carbonyl compounds.[22] In chromium carbonyl derivatives, ligands which have a high σ-donor : π-acceptor ratio tend to increase the electron density on the chromium atom, which implies a higher π-back bonding to the *trans*-carbonyl group. The decrease of the *trans*-Cr–C distance and the consequent increase of the *trans*-C–O distance[22] of **1** show the tendency of the cyanamide ligand to increase the negative charge on the metal [Cr(CO)$_5$L] complexes with L possessing a high σ-donor : π-acceptor ratio have short Cr–C distances ($\approx$ 180 pm) and long C–O distances ($\approx$116 pm), while complexes incorporating a ligand with a low σ-donor : π-acceptor ratio tend to have long Cr–C$_{trans}$ and short *trans*-C≡O distances ($\approx$192 and 114 pm, respectively). Therefore, the diethylcyanamide ligand has a stronger σ-donor : π-acceptor ratio than the carbonyl group. In the [Cr{=C(OEt)Me}(CO)$_5$] complex,[23] the Cr–C$_{trans}$ distance is longer than in **1** and thus indicates that cyanamide has a stronger σ-donor : π-acceptor ratio than the carbene ligand.

Only X-ray diffraction data are available for [Cr(CO)$_5$L] compounds where L is a ligand bonded by different nitrogen atoms. For these compounds the Cr–C$_{trans}$ distances decrease with increasing hybridization of the nitrogen atom; *e.g.*, 180.4(9)–181.9(6) for sp^3,[24,25] 181.6(9)–182.9(4) for sp^2[26,27] and 182.1(4)–185.0(3) pm for sp nitrogen hybridization.[28] The σ-donor : π-acceptor ratio decreases in the order sp > to > sp^2 and > sp^3, in which the nitrogen atom has respectively 2, 1 and 0 π* orbitals available for back donation. The values for the sp hybridized N of **1** obtained by neutron [185.0(3)] and by X-ray diffraction [182.9(4) pm] agree with the ranges above. The classification of the σ-donor : π-acceptor capacity of the ligands (in the order sp^{3}N > sp^{2}N > spN > carbene > CO) as derived from the Cr–C$_{trans}$ distances is in good agreement with the chemical properties of these ligands.[29]

Preferential Orientation of the cis-*Carbonyl Groups.*—Kostic and Fenske[30] have shown by theoretical means that carbonyl groups are oriented towards the groups with the weakest π-acceptor character. Thus, the four *cis*-carbonyl groups of **1** should be bent towards the cyanamide ligand. However, in **1** only the C(2)O(2) carbonyl groups are directed towards this ligand [N(α)–Cr–O(2) 88.5(1)°], whereas the other two, C(3)-O(3), are shifted towards the *trans*-carbonyl group, C(1)O(1) [N(α)–Cr–O(3) 94.3(1)°]. This difference can be explained by examining the two planes separately and by taking into account the presence of the mesomer form N(α)=C(β)=N(γ). Let *xz* be the plane N(α)C(β)N(γ)C(4)$_2$ which contains the C(2)O(2) groups [Fig. 3(*a*)]. There is the possibility of overlap of the π$_x$* orbitals of N(α)C(β) and the π* orbital formed by classical σ donation–π-back donation of the Cr(CO)$_4$ group [Fig. 3(*c*)] described by Chatt *et al.*[31] giving rise to a shift of the C(2)O(2) groups towards the cyanamide ligand. This deformation is even more important when the nitrogen atom has more positive character. On the contrary, in the perpendicular *yz* plane [Fig. 3(*b*)], the double bond is situated between C(β) and N(γ), and the overlap is then less pronounced for the p$_y$ electron pair.

Table 2 Interatomic distances, bond angles and torsion angles of $[Cr(NCNEt_2)(CO)_5]$ at 110 K (neutron diffraction) and 243 K (X-ray diffraction[4])*

	T/K			T/K	
	110	243		110	243
Cr–C(1)	185.0(3)	182.9(4)	C(β)–N(γ)	130.4(2)	131.4(5)
Cr–C(2)	191.1(1)	189.5(3)	N(γ)–C(4)	147.2(1)	146.0(4)
Cr–C(3)	191.6(1)	189.1(4)	C(4)–C(5)	151.1(2)	149.3(6)
C(1)–O(1)	115.4(3)	116.4(5)	C(4)–H(41)	109.6(4)	91.6
C(2)–O(2)	114.3(2)	114.1(4)	C(4)–H(42)	109.8(4)	104.5
C(3)–O(3)	113.8(2)	113.8(5)	C(5)–H(51)	108.8(4)	96.6
Cr–N(α)	206.3(3)	206.3(3)	C(5)–H(52)	108.9(4)	92.8
N(α)–C(β)	116.7(2)	113.9(5)	C(5)–H(53)	109.5(4)	97.1
C(1)–Cr–C(2)	91.4(1)	91.6(1)	C(4)–N(γ)–C(4^{I})	117.8(1)	117.8(1)
C(1)–Cr–C(3)	87.3(1)	88.0(1)	N(γ)–C(4)–H(41)	107.4(2)	107.2
C(2)–Cr–C(3)	89.3(1)	89.9(1)	N(γ)–C(4)–H(42)	107.5(2)	99.6
C(2)–Cr–N(α)	88.6(1)	88.4(1)	H(41)–C(4)–H(42)	106.6(3)	110.8
C(3)–Cr–N(α)	92.7(1)	92.0(1)	C(5)–C(4)–H(41)	110.8(2)	109.4
Cr–C(1)–O(1)	180.0	180.0	C(5)–C(4)–H(42)	111.2(2)	115.2
Cr–C(2)–O(2)	179.5(2)	178.8(3)	C(4)–C(5)–H(51)	111.5(2)	
Cr–C(3)–O(3)	175.6(1)	175.0(3)	C(4)–C(5)–H(52)	112.2(2)	
C(1)–Cr–N(α)	180.0	180.0	C(4)–C(5)–H(53)	109.8(2)	
Cr–N(α)–C(β)	180.0	180.0	H(51)–C(5)–H(53)	107.9(3)	
N(α)–C(β)–N(γ)	180.0	180.0	H(52)–C(5)–H(53)	108.2(3)	
C(β)–N(γ)–C(4)	121.1(1)	121.1(2)	H(52)–C(5)–H(51)	107.1(3)	
N(γ)–C(4)–C(5)	113.0(1)	114.1(2)			

* The equation of the mean plane, defined by Cr, C(2), C(3), C(2^{I}) and C(3^{I}) atoms, is: $-0.0004x + 0.9993y + 0.0373z - 1.8582 = 0$; symmetry code I $-x, y, \frac{1}{2} - z$.

Table 3 Intermolecular distances (pm) and angles (°) of $[Cr(NCNEt_2)(CO)_5]$ at 110 K (by neutron diffraction)*

	C–H	H···O	C···O	C–H···O
C(5^{II})–H(52^{II})···O(2)	108.9(4)	248.3(4)	352.1(2)	159.1(3)
C(4^{III})–H(41^{III})···O(3)	109.6(4)	269.6(4)	339.9(3)	121.4(2)
C(5^{V})–H(51^{V})···O(2)	108.8(4)	269.8(4)	376.9(3)	168.2(3)
C(5^{III})–H(51^{III})···O(3)	108.8(4)	272.9(4)	329.9(3)	112.3(2)
C(4^{IV})–H(41^{IV})···O(1)	109.6(4)	278.2(4)	334.4(2)	111.6(2)
C(4^{IV})–H(42^{IV})···O(1)	109.8(4)	298.1(4)	334.4(2)	99.6(2)

* Translation codes: II $x + \frac{1}{2}, y - \frac{1}{2}, z + 1$; III $x + \frac{1}{2}, y - \frac{1}{2}, z$; IV $x, y - 1, z$. Symmetry code: V $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$.

The repulsion between the p_y lone pair of N(α) and the π lone pair of the C(3)O(3) carbonyl groups results in the latter moving away from the cyanamide ligand.

The Chromium–Nitrogen Bond.—Fig. 4 shows the different Cr–N distances as a function of the hybridization of the nitrogen atom. Two classes of compound are considered: the first involving ligands where the nitrogen atom keeps its lone pair (**I**–**IV**), the second incorporating ligands where all the electrons of the nitrogen atom are involved in bonding (**V**–**VIII**). Only one chromium–nitrogen triple bond (**I**) was reported by Orpen *et al.*[32] The observed value[33] [156.5(6) pm] agrees with the theoretical Cr≡N distance [159(2) pm] calculated by Nugent and Haymore[45] from the relative metallic sizes defined by Pauling.[45a] The chromium–nitrogen double bond (**II** and **V**) in the Cr=N=O group has an average value of 168.4(2.2) pm for 16 structures.[32] The 'single' Cr–N bonds (**III**, **IV**, **VI**, **VII** and **VIII**) are, as expected,[46] distributed over a wide range (198–245 pm) depending on the hybridization and the environment of the nitrogen atom, the Cr–N distances increasing in the order spN < sp^2N < sp^3N. This is in agreement with the reduction of the capacity for chromium-to-nitrogen back-donation which is in the order: sp > sp^2 > sp^3. However, within each series, the nature of the ligand *trans* to the nitrogen atom should also be considered. For example, for sp^3N, the $Cr–N_{amine}$ distances differ significantly when the amine group is *trans* to NH_3 [207.7(2)], F [209.3(6)] and CO [219.5(4) pm].[47–49] Therefore, for a good comparison, only compounds with the same *trans* ligand may be considered. Taking this into account and recalling the discussion of the *trans* effect above, a comparison can be made by plotting $d[Cr–(CO)_{trans}]$ *versus* d(Cr–N) for different compounds (Fig. 5). Although the overall variation is small, three separate groups of representative points are observed. The first group [(*a*)–(*h*)] corresponds to compounds with a four-co-ordinate nitrogen (sp^3N) with a single bond to chromium, the second [(*i*)–(*k*)] and third [(*l*)–(*p*)] groups to compounds involving sp^2N and spN-bonding atoms respectively. The characteristics of these bonds may be investigated in more detail. For the first group, one can check that the distances agree with the classical estimation of the single Cr–N(sp^3) bond in which the amine nitrogen atom has no π-bonding orbital, as carried out by Cotton and Richardson.[40] The observed average value [219(1) pm] is in accord with the sum of the covalent radii,* *i.e.* r(Cr) + r(sp^3N) = 146 + 73 = 219 pm. Similarly single Cr–N(sp^2) and Cr–N(sp) bonds should be 217 (146 + 71) and 215 (146 + 69) pm respectively.† The average experimental value for **1** and the other compounds [(*l*)–(*p*)] [206(1) pm] is significantly shorter than the calculated distance for a pure single Cr–N(sp) bond, showing there is definitely a π-back-donating contribution in these compounds.

---

* The chromium covalent radii is taken from ref. 53, whilst the covalent radii of sp^3N, sp^2N and spN are deduced from ref. 54.

† The difference between r(sp^3N) and r(spN) is 4 pm. Carter *et al.*[55] have suggested a value of 6 pm for this difference but no explanation was given for the origin of this value.

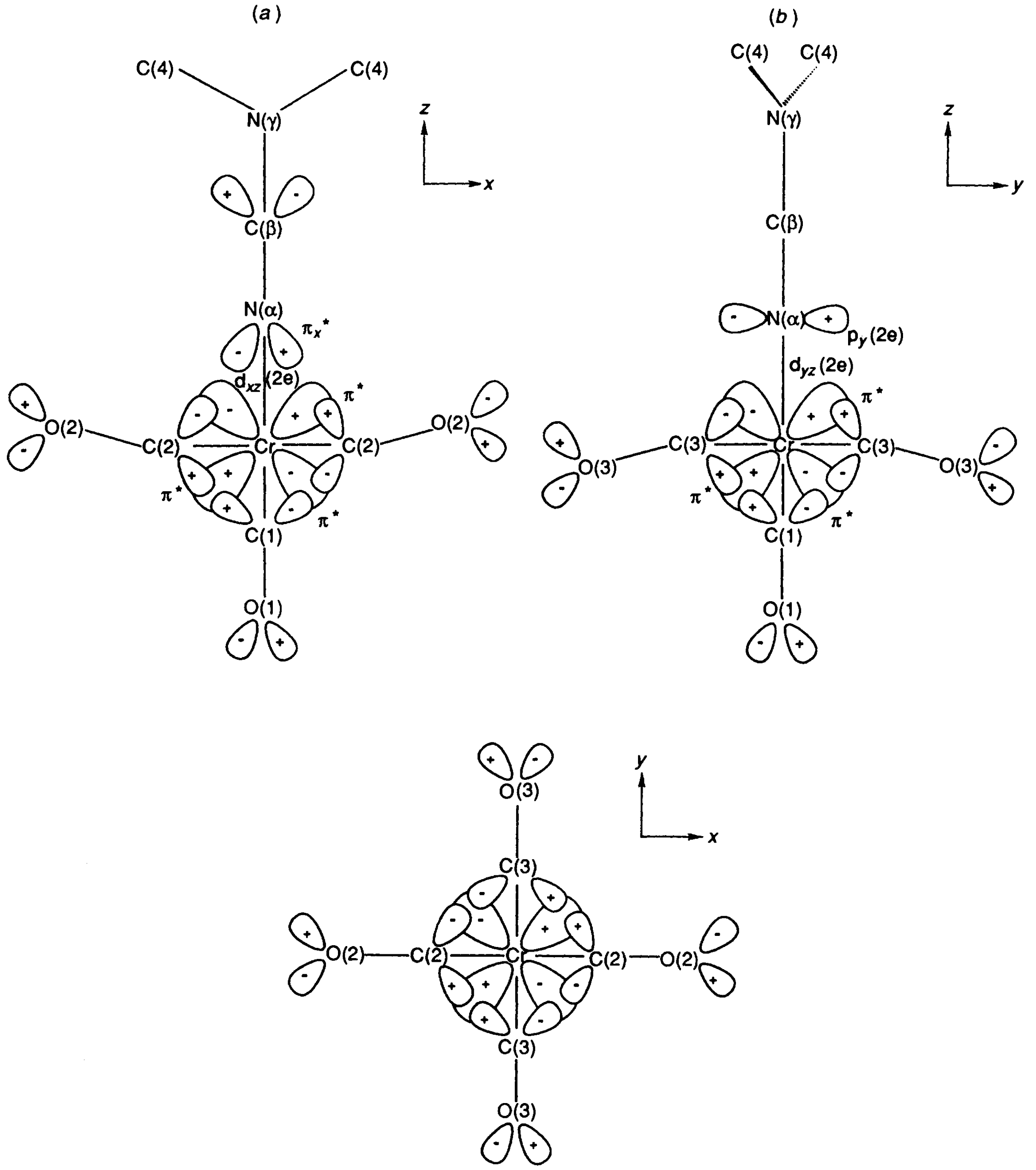

Fig. 3 Possible overlap of chromium d orbitals with the corresponding ligand orbitals in the relevant plane: (*a*) d_{xz} orbitals, N(γ)CrC(2) (*xz*) plane; (*b*) d_{yz} orbitals, N(γ)CrC(3) (*yz*) plane; (*c*) d_{xy} orbitals, C(2)CrC(3) (*xy*) plane

Comparison with Other Compounds containing the Cyanamide Ligand.—The C(β)–N(γ) bond distance in the cyanamide ligand in **1** [130.4(2) pm] is similar to that deduced for N(3)–C[sp]* [131(1) pm]; also, the ethyl group distances N(γ)–C(4) [147.2(1)] and C(4)–C(5) [151.1(2) pm] are in good agreement with the average values for N(3)–C(sp^3) and C(sp^3)–C(sp^3) bonds,[54] 146(1) and 151(1) pm respectively. The N(α)≡C(β) triple bond in **1** [116.7(2) pm] is slightly longer than the N(2)≡C(sp) bonds [⟨114.4(6)⟩ pm]. This difference may be attributed to shorter triple bond distances being observed in structures determined by X-ray diffraction compared to those determined by neutron diffraction (see above).

The cyanamide ligand skeleton is planar, with the N(γ) atom sp^2 hybridized. To our knowledge, there are no structural data in the literature for diethylcyanamide and its conformation is still unknown. However, the structures of $NCNH_2$ and of $NCNMe_2$ have been studied by neutron and X-ray diffraction in the solid state,[19,20] and by electron diffraction (for $NCNMe_2$)[56] and also by vibrational and microwave spectroscopy in the liquid and gaseous states[57] respectively. The N(γ) atom in both compounds has sp^3 hybridization: the observed, out-of-plane angle θ, varies between 8 and 35°. *Ab initio* calculations were also carried out for these molecules in order to understand the packing effect.[58] The angle θ decreases to about 15° when the skeleton has 12 neighbours and is very close to the experimental value observed in the solid state.[20] This suggests that when diethylcyanamide forms a complex with the $Cr(CO)_5$ group, complete delocalization of the electron pair on the N(γ) atom is

---

* Allen *et al.*[54] have not quoted bonds such as N(3)–C(sp) or N(3)=C(sp)=. From the C(sp)–C(sp), C(sp^2)–C(sp) and C(sp^2)–C(sp^2) distances [138(1), 143(1) and 148(1) pm, respectively] it is observed that there is an increase of about 5 pm upon substitution of an spC by an sp^2C atom. The N(3)–C(sp) distance was determined by taking the corresponding N(3)–C(sp^2) distance [136(1) pm] and subtracting 5 pm to give 131(1) pm. Here, *n* in N(*n*) represents the co-ordination number of the nitrogen atom (see Fig. 4).

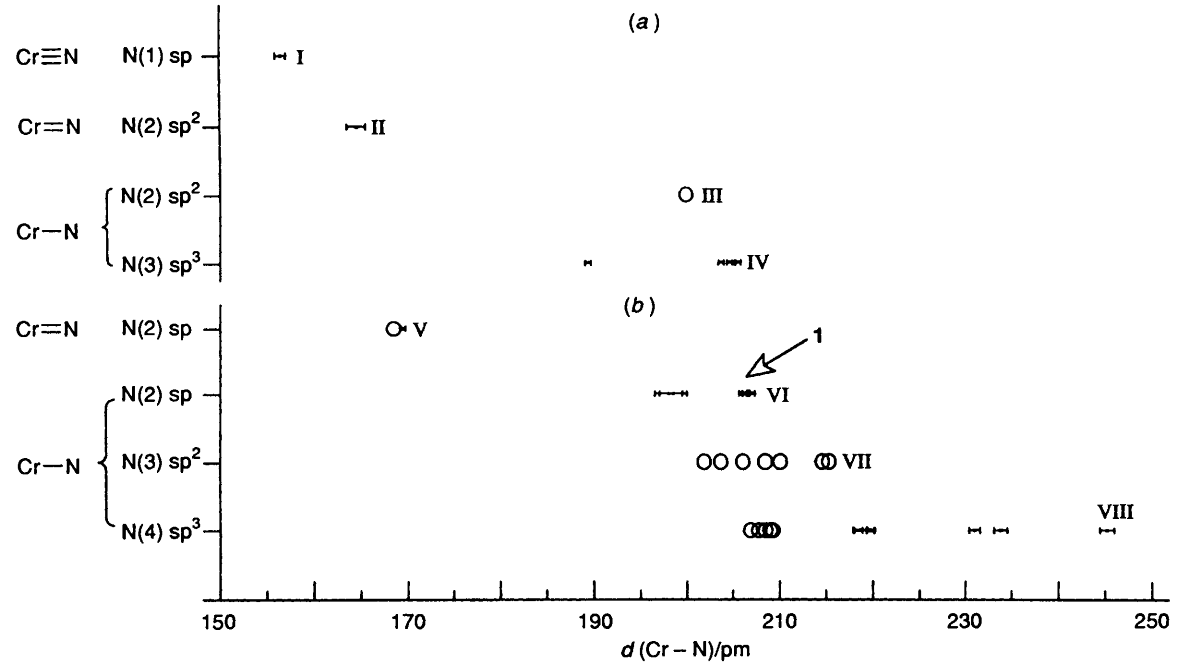

Fig. 4 Observed Cr–N bond lengths for a series of characteristic complexes with (*a*) and without (*b*) a lone pair on nitrogen. The numbers 1–4 represent the co-ordination number of the nitrogen atom. The average Cr–N distances (○) were obtained from a study compiled using the Cambridge Database[32] with additional values taken from refs. 33(**I**), 34(**II**), 35(**IV**), 36(**V**), 4, 28, 37–39(**VI**) and 25, 26, 40–43(**VIII**), for cases where the nitrogen environment was not included in ref. 32

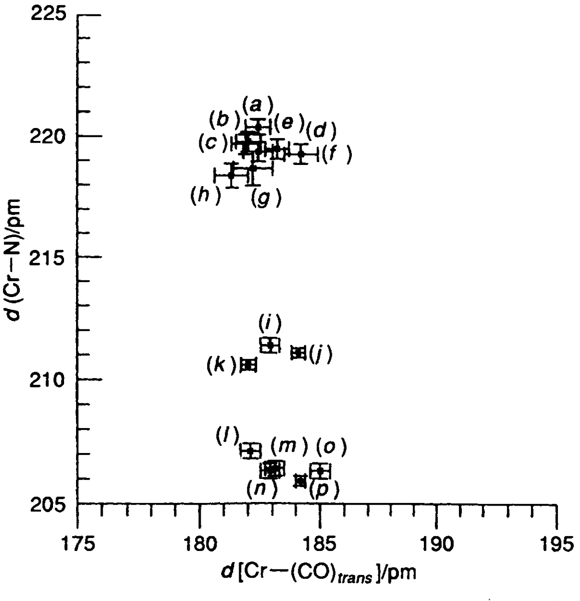

Fig. 5 Variation of the chromium–nitrogen interatomic distance *versus* the chromium–carbon$_{trans}$ interatomic distance for the compounds [Cr(CO)$_x$L], where x = 3–5: (*a*) [Cr($C_5H_{10}NH$)$(CO)_5$],[50] (*b*) [CrL$(CO)_4$],[43] (where L = *N,N′,N″,N‴*-tetramethyl-2,2′-biimidazolidin-2-ylidene), (*c*) [Cr(C_4H_9NO)$(CO)_5$],[25] (*d*) [Cr($NHMe_2$)$(CO)_5$],[49] (*e*) [Cr(C_5H_5N)(CO_5],[50] (*f*) [Cr{P$(OMe)_3$}($C_5H_{10}NH$)$(CO)_4$],[50] (*g*) Cr–NH and (*h*) Cr–NH_2 in [Cr(dien)$(CO)_3$][40] (where dien = diethylenetriamine), (*i*) [Cr($C_3H_4N_2Se$)$(CO)_5$],[27] (*j*) [Cr($C_3N_3H_5$)$(CO)_5$],[51] (*k*) [Cr($C_8H_6N_4$)$(CO)_4$]·$C_8H_6N_4$,[52] (*l*) [Cr{NCN=C(CO_2Et)N(H)C_6H_4Cl-4}$(CO)_5$],[28] (*m*) [Cr(NCSMe)$(CO)_5$],[49] (*n*) **1**,[4] (*o*) **1** (this work) and (*p*) [Cr(NCSMe)$(CO)_5$][37]

possible, giving rise to the sp^2 hybridization. In other organometallic complexes found in the literature {*e.g.* [$Mo_2(OCH_2Bu^t)_6(\mu\text{-}C_4Me_4)(NCNEt_2)$][59] **2**, and Sb[NCN$(CHMe_2)_2$]$Cl_5$[60] **3**} this is the only conformation which has been observed. In all three complexes, the N(α)–C(β), C(β)–N(γ) and N(γ)–C(R) distances are quite comparable (Table 4). However, the MN(α)C(β)N(γ) part is linear for **1** and **2** whereas M–N(α)–C(β) is 133(1)° for **3**.

Bond Orders.—From the bond lengths, it is possible to estimate the bond order for some characteristic bonds of **1**, using the procedure detailed in ref. 61. It has already been noted that the four *cis*-Cr–C(carbonyl) distances in **1** have the same value as in [Cr$(CO)_6$]. Their bond orders are the same (each 1.5). There remain three bond order units for the Cr–C$_{trans}$ and the Cr–N distances if one assumes that the back-donation effect of the Cr atom is the same for C and N atoms. The Cr–C$_{trans}$ distance has been found to be 185 pm. It is generally accepted that for bond orders in the range 1–2 there is a variation of *ca.* 30–40 pm per bond order unit for a Cr–C distance. With a shortening of 6.8 pm, the Cr–C$_{trans}$ bond order is then estimated to be 1.73–1.67, giving Cr–N a bond order of 1.28–1.33. This shows that there is a π contribution from the nitrogen atom of the cyanamide moiety to the Cr atom in good agreement with the independent conclusion drawn above.

The bond order can also be estimated from a correlation curve established using the Schomaker and Stevenson[62] covalent radius, corrected for the electronegativity effect.[45b] Using the results for **1** obtained here bond order values of 1.7 and 1.3 are obtained for the Cr–C$_{trans}$ Cr–N(α) bonds respectively, which are in good agreement with those above. Bond orders for N(α)–C(β), C(β)–N(γ) and N(γ)–C* are found to be 2.6, 1.7 and 1 respectively.

Hydrogen Bonding.—Since the structure of **1** solved by neutron diffraction gives accurate positions of the hydrogen atoms, it is possible to discuss precisely the nature of the intermolecular bonding in this compound. Considering first the C–H distances of the ethyl groups, these are equal within the limits of experimental error. The distances between the two

---

* The formal bond order of the C(β) carbon is slightly greater than 4. According to Weatley,[63] estimation of bond order is difficult for the adjacent π bond. Thus, all such estimated bond orders are assumed to have *ca.* 10% error.

Table 4 Interatomic distances (pm) of the cyanamide fragment in complexes or salts containing the $NCNR_2$ (R = Et **1** and **2**, R = $CHMe_2$ **3**) ligand. The out-of-plane angle, θ, is defined by the C(β)–N(γ) bond with the N(γ)R_2 plane

Compound	N(α)–C(β)	C(β)–N(γ)	N(γ)–C(R)	θ/°	Ref.
1[a]	113.9(5)	131.4(5)	146.0(4)	0	4
1[b]	116.7(2)	130.4(2)	147.2(1)	0	this work
2[c]	114.6(8)	131.7(8)	147.4(9)	19.7(4)	59
3[d]	117(2)	129(2)	150(2)	13(1)	60

[a] Determined by X-ray diffraction, 243 K. [b] Determined by neutron diffraction, 110 K. [c] Determined by X-ray diffraction, 169 K. [d] Determined by X-ray diffraction, 298 K.

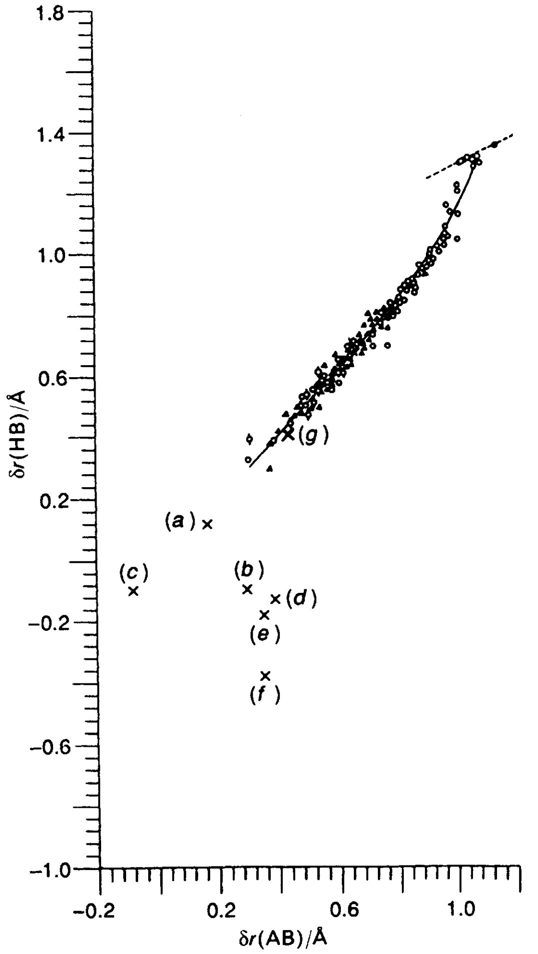

Fig. 6 Criterion for the existence of hydrogen bonds.[65]: (a)–(f) correspond to the C–H ··· O contacts in Table 3 lettered in the order of the table, (g) corresponds to the complex $[Cr{\equiv}CC_6H_5)Cl(CO)_4]$,[17a] ●, O–H···F; ■, O–H···N; ○, O–H···O; ⌽, O–H···Cl; ×, N–H···N; △, N–H···O; ▲, N–H···Cl; ◑, F–H···F

heavy atoms in the hydrogen bond (*i.e.* C or O) are all longer by at least 30 pm than the length suggested by Hamilton and Ibers[64] (based on van der Waals radii) which indicate the existence of a hydrogen bond. Therefore it is difficult to claim that any of the ethyl hydrogens are more involved in hydrogen bonding than the others. It is also well known that C–H distances of ethyl groups are affected very little by hydrogen bonding, and it is thus difficult to identify hydrogen bonding in this way. However, the direct distance between hydrogen and oxygen atoms for the C–H···O bond, *e.g.* in the $C(5^{II})$–$H(52^{II})$···O(2) bond, the $H(52^{II})$···O(2) distance is 248.3(4) pm, which is significantly less than the van der Waals distance (260 pm).[64] All the other H··· O distances are longer than this value (Table 3).

Rahim and Barman[65] have introduced a more sophisticated criterion based on relations linking the hydrogen-bonding distances and have checked them for more than 130 neutron structures. The relationship between δ*r*(HB) and δ*r*(AB) for a hydrogen bonded A–H··· B system is defined as in equations (3) and (4) where *w*(X) is the van der Waals radius of the atom

$$\delta r(\mathrm{HB}) = w(\mathrm{H}) + w(\mathrm{B}) - d(\mathrm{H{-}B}) \qquad (3)$$

$$\delta r(\mathrm{AB}) = r(\mathrm{A{-}H}) + w(\mathrm{H}) + w(\mathrm{B}) - d(\mathrm{A{-}B}) \qquad (4)$$

X, *d*(X–Y) the observed distance between the X and Y atoms and *r*(X–Y) the length of the covalent bond X–Y.[65] Fig. 6 shows the refined relationship and the experimental data for well known hydrogen-bonding systems. Using this relation for all the C–H bonds in **1**, most of the points do not fit the curve, except that for $C(5^{II})$–$H(52^{II})$···O(2) which lies within the limits of experimental error. As Rahim and Barman[65] did not report any results for C–H···O contacts we also plot a value for the compound $[Cr({\equiv}CC_6H_5)Cl(CO)_4]$,[17a] in which C–H··· Cl contacts were found to involve a strong hydrogen bond. For this compound, the representative point also fits the curve. These facts demonstrate that the $C(5^{II})$–$H(52^{II})$···O(2) bond is hydrogen bonding in nature, while the other contacts are van der Waals bonds.

Fig. 2 represents the packing of molecules of **1** in the crystal. The molecules are distributed on layers parallel to the $\vec{b}$, $\vec{c}$ plane which is in fact the twin plane, with an interlayer separation of *ca.* 78 pm. In addition to the van der Waals interactions, the structure is held together by hydrogen bonds linking the molecules of different layers approximately parallel to the direction $\vec{c} + \vec{a}/2$.

Conclusion

The resolution of the crystal structure of **1** by neutron diffraction at 110 K was slightly problematic because the crystal used was twinned. Nevertheless, after a precise analysis of the two twin elements, the structure refinement converged to give a satisfactory model.

The crystal structure comprises layers of molecules parallel to the $\vec{b}$, $\vec{c}$ plane (the twin plane) and in addition to van der Waals interactions, the molecules are held together by intermolecular hydrogen bonds.

Situated on the binary axis of the space group *C*2/*c*, the molecule has C_{2v} symmetry and shows various hybridization of the orbitals with respective mirror symmetries. The two *cis*-carbonyl groups play different roles in terms of the conjugation effect. In a comparison with single chromium–nitrogen bonds in related complexes, the Cr–N(sp) bond is shown to have a π contribution. The diethylcyanamide ligand, which has a planar skeleton, induces a strong delocalization of the sp^2N lone pair on the C(sp)–N(sp^2) bond; also, it is found to have an intermediate σ-donor:π-acceptor ratio, which is stronger than the carbene ligand. The bond orders of the linear chain are determined: 1.7 for Cr–C_{trans}, 1.3 for Cr–N(α), 2.6 for N(α)–C(β) and 1.7 for C(β)–N(γ). The molecular structure of the cyanamide ligand in **1** is very similar to that of other cyanamide ligands in related compounds which have a σ nitrogen–metal bond and various M–N(α)–C(β) angles.

Acknowledgements

Some calculations were carried out on the SUN and CONVEX computers of the Laboratoire Léon Brillouin. M.-N. O. and A. S.-de B. thank the system team for their technical support. The authors also thank Dr. T. Prangé of the Laboratoire de Chimie Structurale Biomoléculaire for his help in the implementation of the graphical programs on the SUN computers of the Laboratoire de Physico-Chimie Moléculaire et Minérale.

References

1 H. Berke, P. Härter, G. Huttner and L. Zsolnai, *Chem. Ber.*, 1982, **115**, 695.

2 H. Fischer, F. Seitz and G. Müller, *Chem. Ber.*, 1987, **120**, 811.

3 F. Seitz, H. Fischer, J. Reide, T. Schöttle and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 744; F. Seitz and M. S. Wrighton, *Inorg. Chem.*, 1987, **26**, 64.

4 E. O. Fischer, W. Kleine, U. Schubert and D. Neugebauer, *J. Organomet. Chem.*, 1978, **149**, C40; U. Schubert, D. Neugebauer and P. Friedrich, *Acta Crystallogr., Sect. B*, 1978, **34**, 2293.

5 H. Fischer, F. Seitz and J. Reide, *J. Chem. Soc., Chem. Commun.*, 1985, 537; H. Fischer, F. Seitz and J. Riede, *Chem. Ber.*, 1986, **119**, 2080.

6 H. Berke, P. Härter, G. Huttner and J. von Seyerl, *J. Organomet. Chem.*, 1981, **219**, 317.

7 H. Berke and P. Härter, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 225; T. K. Mondal, T. K. Banerjee and S. Debabrata, *Indian J. Chem., Sect. A*, 1980, **19**, 846; F. Seitz, Dissertation, Universität München, 1984.

8 F. Seitz, H. Fischer, J. Reide and J. Vogel, *Organometallics*, 1986, **5**, 2187.

9 H. Berke, G. Huttner and J. von Seyerl, *Z. Naturforsch., Teil B*, 1981, **36**, 1277.

10 A. Spasojevic-de Biré, Nguyen Quy Dao, A. Strich, C. Thieffry, M. Bénard, *Inorg. Chem.*, 1990, **29**, 4908; A. Spasojevic-de Biré, Nguyen Quy Dao, E. O. Fischer and N. K. Hansen, *Inorg. Chem.*, 1993, **32**, 5354.

11 G. P. Foulet-Fonseca, M. Jouan, Nguyen Quy Dao, H. Fischer, J. Schmid and E. O. Fischer, *Spectrochim. Acta, Part A*, 1990, **46**, 339; G. P. Foulet-Fonseca, M. Jouan, Nguyen Quy Dao, N. Tran Huy and E. O. Fischer, *J. Chem. Phys.*, 1990, **87**, 13.

12 U. H. Zucker, E. Perenthaler, W. F. Kuhs, R. Bachmann and H. Schulz, *J. Appl. Crystallogr.*, 1983, **16**, 358.

13 L. Koester, *Springer Tracts in Modern Physics, Neutron Physics*, ed. G. Höhler, Springer, Berlin, 1977, vol. 20, p. 36.

14 P. Becker, *Acta Crystallogr., Sect. A*, 1977, **33**, 243; P. Becker and P. Coppens, *Acta Crystallogr., Sect. A*, 1974, **30**, 129.

15 C. K. Johnson, ORTEP II program, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

16 S. Motherwell and W. Clegg, PLUTO program, University of Cambridge, 1978.

17 (*a*) Nguyen Quy Dao, D. Neugebauer, H. Février, E. O. Fischer, P. J. Becker and J. Pannetier, *New J. Chem.*, 1982, **6**, 359; A. Frank, E. O. Fischer and G. Huttner, *J. Organomet. Chem.*, 1978, **161**, C27.

18 J. L. Petersen, R. K. Brown and J. M. Williams, *Inorg. Chem.*, 1981, **20**, 158.

19 N. K. Hansen, L. Dyhr-Nielsen and F. K. Larsen, *Abstracts American Crystallographic Association, Winter Meeting, Clemson, SC*, 1976, **4**, 28; L. Dyhr-Nielsen, N. K. Hansen and F. K. Larsen, Danish Crystallographic Meeting, Århus, 1975.

20 L. Denner, P. Luger and J. Buschmann, *Acta. Crystallogr., Sect. C*, 1988, **44**, 1979.

21 A. Jost, B. Rees and W. B. Yelon, *Acta Crystallogr., Sect. B*, 1975, **31**, 2649.

22 S. W. Kirtley, *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. Stone and E. Abel, Pergamon, New York, 1982, vol. 3, p. 806.

23 C. Krüger, R. Goddard and K. H. Claus, *Z. Naturforsch., Teil B*, 1983, **38**, 1431.

24 F. A. Cotton and M. D. Laprade, *J. Am. Chem. Soc.*, 1969, **91**, 7000.

25 M. L. Rodrigez, I. Brito, F. V. Rodrigez-Romero, V. Manriquez, G. Gonzalez and C. Diaz, *Acta Crystallogr., Sect. C*, 1991, **47**, 858.

26 T. Sielisch and U. Behrens, *J. Organomet. Chem.*, 1986, **310**, 179.

27 V. Bätzel and R. Boese, *Z. Naturforsch., Teil B*, 1981, **36**, 172.

28 U. Eckert, C. Robl and W. P. Fehlhammer, *Organometallics*, 1993, **12**, 3241.

29 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335; B. N. Storhoff and H. C. Lewis, jun., *Coord. Chem. Rev.*, 1977, **23**, 1.

30 N. M. Kostic and R. F. Fenske, *J. Am. Chem. Soc.*, 1981, **103**, 4677.

31 J. Chatt, A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4456.

32 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

33 J. T. Groves, T. Takahashi and W. M. Butler, *Inorg. Chem.*, 1983, **22**, 884.

34 N. Wiberg, H. W. Häring and U. Schubert, *Z. Naturforsch., Teil B*, 1978, **33**, 1365.

35 G. A. Sim, D. I. Woodhouse and G. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1979, 83; M. Soriano-Garcia, J. Valdes-Martinez, R. A. Toscano and J. Gomez-Lara, *Acta Crystallogr., Sect. C*, 1985, **41**, 500; W. T. Pennington, A. W. Cordes, D. Kyle and E. W. Wilson, jun., *Acta Crystallogr., Sect. C*, 1984, **40**, 1322.

36 T. V. Greenhough, B. W. S. Kolthammer, P. Legzdins and J. Trotter, *J. Chem. Soc., Chem. Commun.*, 1978, 1036.

37 R. Goddard, S. D. Killops, S. A. R. Knox and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 1255.

38 B. J. Helland, M. H. Quick, R. A. Jacobson and R. J. Angelici, *J. Organomet. Chem.*, 1977, **132**, 95.

39 F. Edelmann and U. Behrens, *J. Organomet. Chem.*, 1977, **131**, 65.

40 F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

41 M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, *Inorg. Chem.*, 1978, **17**, 3536.

42 F. A. Cotton and G. W. Rice, *Inorg. Chem.*, 1978, **17**, 2004.

43 P. B. Hitchcock, M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2160; B. Cetinkaya, P. B. Hitchcock, M. F. Lappert and P. L. Pye, *J. Chem. Soc., Chem. Commun.*, 1975, 683.

44 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.

45 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY, 1960, (*a*) p. 256; (*b*), pp. 224–228.

46 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.

47 T. P. Haromy, W. B. Knight, D. Dunaway-Mariano and M. Sundaralingam, *Acta Crystallogr., Sect. C*, 1984, **40**, 223.

48 K. A. Beveridge, G. W. Bushnell and A. D. Kirk, *Acta Crystallogr., Sect. C*, 1985, **41**, 899.

49 R. D. Rogers and H. G. Alt, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 533.

50 L. A. Cotton, D. J. Darensbourg, A. Fang, B. W. S. Kolthammer, D. Reed and J. Lon Thompson, *Inorg. Chem.*, 1981, **20**, 4090.

51 G. Vos, J. G. Haasnoot, G. C. Verschoor, C. Long and J. G. Vos, *J. Organomet. Chem.*, 1982, **231**, 315.

52 R. M. Buchanan, C. Bauch and D. E. Williams, *Acta Crystallogr., Sect. C*, 1989, **45**, 336.

53 V. G. Andrianov, B. P. Biryukov and Y. T. Struchkov, *Zh. Strukt. Khim.*, 1969, **10**, 1129; *J. Struct. Chem.* (*Engl. Transl.*), 1969, **10**, 1014.

54 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

55 O. L. Carter, A. T. McPhail and G. A. Sim, *J. Chem. Soc. A*, 1966, 1095.

56 L. S. Khaikin, L. V. Vilkov, L. G. Andrutskaya and A. Zenkin, *J. Mol. Struct.*, 1975, **29**, 171.

57 H. D. Blackwood, jun., Ph.D. Thesis, Clemson University, SC, 1974; M. Birk and M. Winnewisser, *Chem. Phys. Lett.*, 1986, **123**, 382; R. D. Brown, P. D. Godfrey, M. Head-Gordon, K. H. Wiedenmann and B. Kleibömer, *J. Mol. Spectrosc.*, 1988, **130**, 213.

58 T. U. Helgaker and B. Klewe, *Acta Chem. Scand., Ser. A*, 1988, **42**, 269.

59 M. H. Chisholm, K. Folting, J. C. Huffmann and N. S. Marchant, *Organometallics*, 1986, **5**, 602; J. C. Huffman, Indiana University Department of Chemistry, Molecular Structure Center, Report No. 84064, 1984.

60 J. C. Jochims, R. Abu-El-Halawa, L. Zsolnai and G. Huttner, *Chem. Ber.*, 1984, **117**, 1161.

61 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn., Interscience, New York, 1972, pp. 684–685.

62 V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, 1941, **63**, 37.

63 P. J. Wheatley, *Acta Crystallogr.*, 1954, **7**, 68.

64 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, Benjamin, New York, 1968, p. 16.

65 Z. Rahim and B. N. Barman, *Acta Crystallogr., Sect. A*, 1978, **43**, 761.

Received 4th July 1994; *Paper* 4/04025B