

Chemical bonding in metalaheterocumulene complexes: II ^{*}

Demonstration of a temperature dependant conformational disorder of the methyl groups in $[(\text{CO})_5\text{CrNCN}(\text{C}_2\text{H}_5)_2]$

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Received 14 June 1994

Abstract

During the determination of the crystal structure of $[(\text{CO})_5\text{CrNCN}(\text{C}_2\text{H}_5)_2]$ by neutron diffraction, a remarkable temperature-dependance of the intensity of three reference reflections between 100 and 300 K was accidentally observed. In order to try to understand the nature of this phenomenon, the behaviour of this compound as a function of the temperature has been studied by differential calorimetry, and by powder and single crystal X-ray diffraction methods. These experiments show neither a phase transition nor a crystal space group modification. The experimental results, supported by a simplified model, suggest a rotational disorder of the methyl groups near room temperature.

Keywords: Chromium; X-ray structure; Neutron structure; Conformational disorder; Metalaheterocumulene

1. Introduction

Over the last few years, metalaheterocumulene chemistry has developed considerably. Allene [2] and 2-aza-allene compounds [3], acetonitrile derivatives [4] and cyanamide [5,6] complexes exhibit charge-transfer phenomena. Some of them have interesting reactivities which, depending on the compound or experimental conditions, can be a substitution reaction [7], an addition to the organic group [8], a modification of the linear chain bonds [9], a nucleophilic attack [10], a photoreaction [2], new complex formation [9], organic syntheses [11], of opening the way to a new catalytic process [11,12].

In order to understand these various chemical properties, an electron deformation density study on the pentacarbonyldiethylcyanamidechromium, $[(\text{CO})_5\text{CrN-}$

$\text{CN}(\text{C}_2\text{H}_5)_2]$, referred to as CrDEC, was undertaken using both X-ray and neutron diffraction experiments. A neutron diffraction study on CrDEC single crystals was made at 110 K [1]. During this experiment, a temperature-dependant phenomena of the intensity of the three neutron reference reflections was accidentally observed between 100 K and 300 K. In order to understand the nature of this phenomenon, some complementary experiments were carried out. These experiments and their interpretations are reported in this paper.

2. Experimental details and results

2.1. Influence of the temperature on CrDEC single crystals, as seen by neutron diffraction

2.1.1. Data collection

The synthesis of the CrDEC crystals and the experimental conditions for data collection on the 5C2 four-

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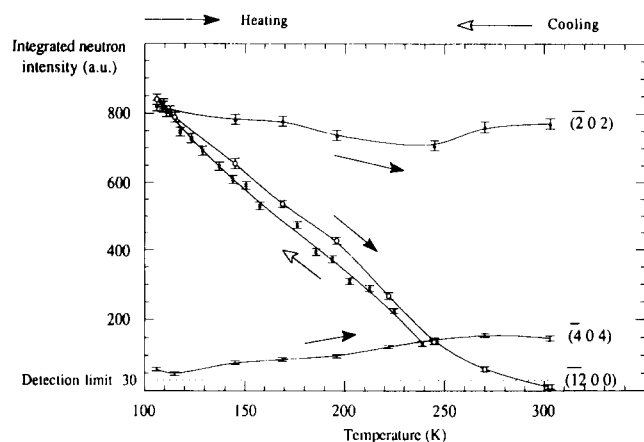


Fig. 1. Temperature-dependence of $(\bar{2} 0 2)$, $(\bar{4} 0 4)$ and $(\bar{12} 0 0)$ neutron intensity reflections. The detection limit of one Bragg reflection is presented as a dotted line.

circle neutron diffractometer of the LLB are described in Ref. 1.

During the neutron experiment it was observed that the $(\bar{12} 0 0)$ intensity, which was very high, vanished when the temperature reached room temperature. Therefore the intensities of three standard reference reflections [$(\bar{4} 0 4)$, $(\bar{12} 0 0)$ and $(\bar{2} 0 2)$] for the neutron data at 110 K [1] were systematically recorded from 100 K to 300 K as the temperature increased (steps of 20 K). The intensity of the $(\bar{12} 0 0)$ reflection was also monitored as the temperature decreased (steps of 10 K).

2.1.2. Results

Fig. 1 represents the $(\bar{2} 0 2)$, $(\bar{4} 0 4)$ and $(\bar{12} 0 0)$ integrated intensity variations – not corrected for the Lorentz and absorption effects – as a function of temperature between 100 K and 300 K. At 303 K, the intensity of the $(\bar{12} 0 0)$ reflection is below the detection limit. Two important points are to be noted: (i) the intensity of the $(\bar{12} 0 0)$ reflection is strong at 100 K, decreases when the temperature increases, and approaches zero near 260 K; this behaviour is reversible, but exhibits a weak hysteresis; (ii) for the other two reflections, the intensity variation is small. (Note that $(\bar{4} 0 4)$ is an harmonic of $(\bar{2} 0 2)$ and their intensities are related.)

2.2. Differential calorimetry of CrDEC from 195 K to 290 K

2.2.1. Experimental details

A differential calorimetric analysis was carried out on a DSC 111-SETARAM calorimeter. Samples were CrDEC crystals of about 10 mm^3 in size. They were placed in an aluminium crucible under dinitrogen. Two crystals were used. Each sample was monitored for

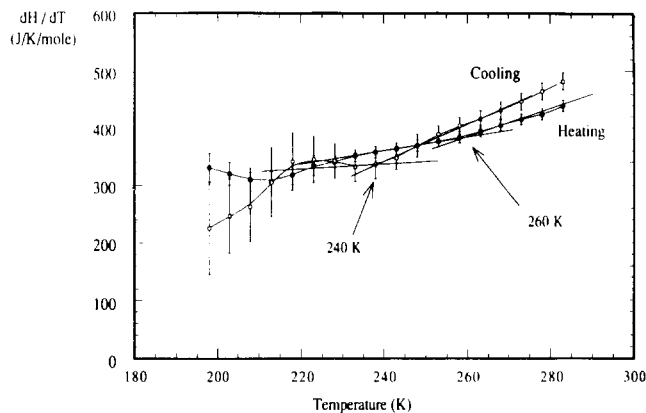


Fig. 2. Temperature-dependence of the OH specific heat of CrDEC.

four cycles between 290 K and 195 K (decreasing and increasing the temperature). This temperature range is imposed by crystal decomposition at the higher temperature (greater than 330 K) and increasing instrumental error below 195 K.

2.2.2. Results

The specific heat of CrDEC (Fig. 2) has been deduced from the mean experimental curves obtained from the four cycles. Two small breaks in the slope of the curves are observed, at $260 \pm 5 \text{ K}$ for the heating curve and near $240 \pm 10 \text{ K}$ for the cooling curve. This “transition” temperature (approximately 260 K) is the same as that observed in the neutron experiment above.

2.3. Cell parameters of CrDEC at 110 K and 300 K by X-ray powder diffraction

2.3.1. Data collection

The X-ray powder diagrams were recorded on a two axes prototype spectrometer ($\lambda_{\text{mean}} = 15.418 \text{ pm}$) [13], using a MERIC cryogenic system (thermal stability $\pm 0.1 \text{ K}$). The sample was ground from CrDEC crystals. X-ray diagrams were recorded at 110 K and 300 K

Table 1

Cell parameter of CrDEC obtained by single crystal neutron diffraction at 110 K [1], by powder X-ray diffraction at 110 K, by single-crystal X-ray diffraction at 293 K, and by X-ray powder diffraction at 300 K

	110 K		293 K	300 K
	crystal Neutron [1]	powder X-ray	crystal X-ray	powder X-ray
a (pm)	1340(3)	1348(3)	1422.6(3)	1422.5(6)
b (pm)	1135(2)	1139.6(9)	1152.0(2)	1152.0(2)
c (pm)	929.1(7)	928(2)	960.7(2)	960.7(5)
β ($^\circ$)	116.08(12)	116.04(15)	118.77(1)	118.81(3)
V (10^9 pm^3)	1.270(18)	1.281(8)	1.380(1)	1.379(2)

K, respectively, for 2θ values varying from 10.61° to 49.43° .

2.3.2. Results

All the Bragg reflections were correctly indexed in the $C2/c$ space group for both diagrams. The cell parameters of CrDEC for the two temperatures (110 K and 300 K) were refined. These values are compared to those obtained from single crystal experiments [5,1] (Table 1). The smallest relative variation corresponds to the b parameter.

2.4. Temperature dependence of a^* and b^* parameters from 85 K to 293 K

2.4.1. Data collection

A X-ray diffraction experiment was conducted on a second two axes diffractometer ($\lambda_{\text{mean}} = 15.418$ pm), with the same cryogenic system. The sample was the crystal used for the neutron diffraction experiment. It was glued with silicone grease under dinitrogen and positioned to have the (\vec{b}, \vec{c}) and (\vec{a}, \vec{c}) planes in reflection position. The Bragg angles 2θ of the $(12\ 0\ 0)$ and $(0\ 10\ 0)$ reflections were measured precisely between 85 K and 293 K (steps of 10 K).

2.4.2. Results

Fig. 3 shows the temperature dependence of $a \sin \beta$ and b cell parameters. There is a regular increase in these two parameters, but no inflection in the curves. The $a \sin \beta$ variation is stronger than that in b , consistent with the powder results.

2.5. Crystal structure of CrDEC single crystal at 293 K by X-ray diffraction

2.5.1. Data collection

These studies were completed by X-ray diffraction measurements made on a CrDEC crystal at 293 K with

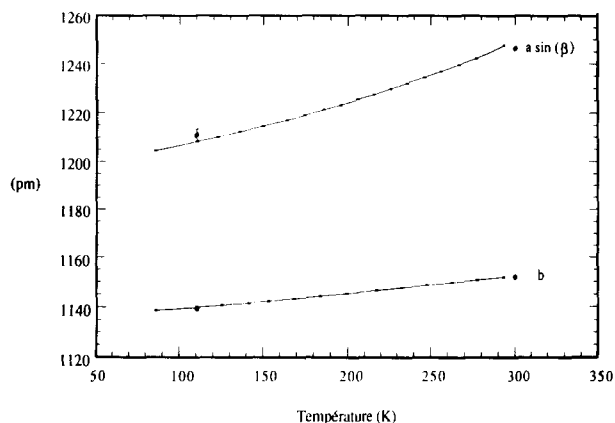


Fig. 3. Temperature-dependence of $a \sin \beta$ and b , by X-ray diffraction on $(12\ 0\ 0)$ and $(0\ 10\ 0)$ faces of a CrDEC crystal. ●: Powder X-ray diffraction at 110 K and 300 K.

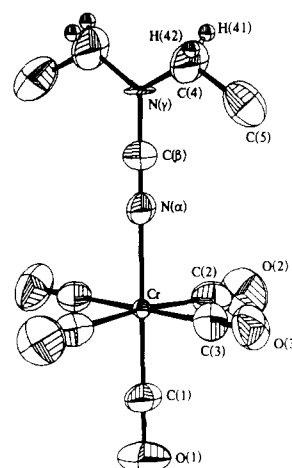


Fig. 4. Molecular structure of CrDEC at 293 K (ORTEP plot [21]).

an ENRAF-NONIUS, CAD-4, four-circle diffractometer ($\lambda_{\text{mean}} = 7.1359$ pm). A CrDEC crystal was cut under dinitrogen in order to separate the visible twin elements [14]. The sample obtained was very small ($0.06 \times 0.02 \times 0.02$ mm³). The crystal was glued to a glass stick, and put in a Lindemann capillary in an inert atmosphere. It decomposed after a four-day experiment, and subsequently no other acceptable crystals were found.

An attempt at structural determination was made from the incomplete dataset (only the reflections with $h \in [0, 11]$, $k \in [\overline{19}, 19]$, $l \in [\overline{16}, 16]$ and $(\sin \theta)/\lambda < 0, 8 \text{ \AA}^{-1}$ were recorded). The four standard reference reflections $((2\ 0\ 0)$, $(\overline{2}\ \overline{2}\ 1)$, $(\overline{1}\ 1\ 1)$ and $(\overline{12}\ 0\ 0)$) (measured every hour) indicated a continuously decreasing intensity totalling 11.6% by the end of the collection. The 6130 measured reflections were corrected for this time-dependence taking into account the decrease of the $(2\ 0\ 0)$ and $(\overline{2}\ \overline{2}\ 1)$ reflection intensities, and for Lorentz-polarisation effect. 3037 average independent reflections had given only 438 reflections with $I > 1\sigma$ [15], with an internal reliability factor $R_{\text{int}} = 9.1\%$ [16].

Using the $I > 1\sigma$ data set and the atomic positions of CrDEC (omitting the hydrogen atoms) determined at 243 K by Fischer et al. [5], the structure was refined with the SHELX76 program [17]. The atomic form factors were taken from the International Crystallographic Tables [18]. The absorption correction (DIFABS program [19]) was carried out giving an average value of $\mu = \langle 0.7 \rangle$ ($\mu_{\text{min}} = 0.13$ and $\mu_{\text{max}} = 1.57$ consistent with the anisotropic experimental condition). The two H(41) and H(42) atoms were localized on the electronic density difference series. However, the positions of the hydrogen atoms of the methyl groups were impossible to determine. The non-hydrogen atoms were refined with anisotropic thermal parameters, and in the final refinement cycle, the weighed reliability factor R_w was equal to 6.6% ($\omega = 0.56/\sigma^2$) with G.O.F. = 2.3 [20].

Table 2

Atomic positions and isotropic thermal parameters of CrDEC at 110 K. $\langle U \rangle = 1/3 \sum U_{ij}(a_i, a_j)(a_i^*, a_j^*)$

Atom	x	y	z	$\langle U \rangle$
Cr	0	0.1578(4)	0.25	0.0016(4)
C(1)	0	0.0008(17)	0.25	0.0052(51)
O(1)	0	-0.1039(12)	0.25	0.0097(60)
N(α)	0	0.3384(16)	0.25	0.0042(35)
C(β)	0	0.4335(19)	0.25	0.0041(46)
N(γ)	0	0.5501(12)	0.25	0.0039(39)
C(2)	0.1075(13)	0.1583(15)	0.4677(16)	0.0054(30)
O(2)	0.1703(8)	0.1615(13)	0.5943(11)	0.0078(26)
C(3)	0.1178(13)	0.1499(17)	0.1841(17)	0.0062(38)
O(3)	0.1728(10)	0.1440(14)	0.1482(15)	0.0106(38)
C(4)	-0.0785(16)	0.6116(12)	0.1187(20)	0.0080(57)
C(5)	-0.1661(15)	0.5481(15)	-0.0139(22)	0.0085(46)
H(41)	-0.0081	0.0646	0.0044	0.0050
H(42)	-0.0110	0.0651	0.0160	0.0050

2.5.2. Crystal structure at 293 K

The complete data collection shows the space group at 293 K to be $C2/c$. The cell parameters are very close to those determined from the X-ray powder diagram at room temperature (Table 1). Atomic parameters, interatomic distances and valence angles of CrDEC at 293 K are presented in Tables 2 and 3. The structural data obtained at 243 K from an X-ray measurement [5] are shown for comparison (Table 3). The molecular structure and the cell representation are given in Figs. 4 and 5.

At the three recorded temperatures (110 K [1], 243 K [5] and 293 K), the general features of the crystal structure of CrDEC are similar. Nevertheless, the thermal parameters seem to be badly resolved at 293 K (Fig. 4) because some ellipsoids do not represent a coherent movement of the molecule. The two C(1)O(1) and C(2)O(2) carbonyl groups exhibit similar interatomic distances at both temperatures (243 K and 293

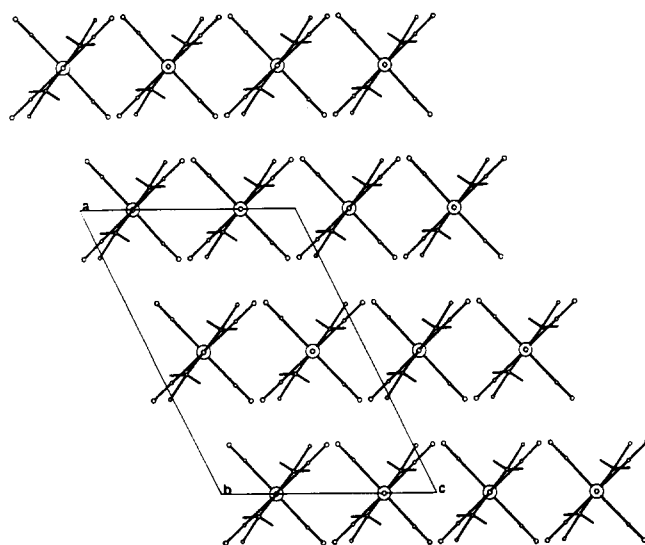


Fig. 5. Projection of the CrDEC crystal structure at 293 K on the \bar{b} axis (PLUTO plot [22]).

K) while the C(3)O(3) group is poorly defined (abnormally long $d(\text{Cr}-\text{C}(3))$ and abnormally short $d(\text{C}(3)-\text{O}(3))$). The Cr-N(α)=C(β)-N(γ) linear chain is similar in both structures (447 pm at 293 K and 451 pm at 243 K) although the N(α)=C(β) distance appears abnormally short.

3. Discussion and conclusion

The various experiments allow some hypotheses on the structural modification of CrDEC as a function of the temperature to be made. First, the space group is the same between 110 K and 300 K. The cell parameters obtained by X-ray powder, and neutron and X-ray single-crystal diffraction methods at both temperatures

Table 3

Interatomic distances (pm), bond angles and torsion angles ($^\circ$) of CrDEC obtained by X-ray diffraction at 293 K and at 243 K [5]. Symmetry code (i): $-x, y, 1/2 - z$

Distances	293 K	243 K	Angles	293 K	243 K
Cr-C(1) <i>trans</i>	180.4(20)	182.9(4)	C(1)-Cr-C(2)	89.9(6)	91.6(1)
Cr-C(2) <i>cis</i>	190.3(14)	189.5(3)	C(1)-Cr-C(3)	87.1(6)	88.0(1)
Cr-C(3) <i>cis</i>	196.8(19)	189.1(4)	C(2)-Cr-C(3)	89.0(7)	89.9(1)
C(1)-O(1) <i>trans</i>	119.7(24)	116.4(5)	C(2)-Cr-N(α)	90.1(6)	88.4(1)
C(2)-O(2) <i>cis</i>	110.9(17)	114.1(4)	C(3)-Cr-N(α)	92.9(6)	92.0(1)
C(3)-O(3) <i>cis</i>	95.3(24)	113.8(5)	Cr-C(2)-O(2)	178.0(15)	178.8(3)
Cr-N(α)	205.3(19)	206.3(3)	Cr-C(3)-O(3)	177.6(18)	175.0(3)
N(α)-C(β)	108.7(28)	113.9(5)	C(β)-N(γ)-C(4)	120.0(11)	121.1(2)
C(β)-N(γ)	133.3(25)	131.4(5)	N(γ)-C(4)-C(5)	120.3(15)	114.1(2)
N(γ)-C(4)	140.5(18)	146.0(4)	C(4)-N(γ)-C(4) ⁽ⁱ⁾	120.0(12)	117.8(1)
C(4)-C(5)	147.4(25)	149.3(6)	N(γ)-C(4)-H(41)	137.3(19)	107.2
C(4)-H(41)	79.0(17)	91.6	N(γ)-C(4)-H(42)	102.8(16)	99.6
C(4)-H(42)	82.6(19)	104.5	H(41)-C(4)-H(42)	107.9(21)	110.8
C(5)-H(51)		96.6	C(5)-C(4)-H(41)	79.0(16)	109.4
C(5)-H(52)		92.8	C(5)-C(4)-H(42)	105.5(18)	115.2
C(5)-H(53)		97.1			

are in good agreement. The $a \sin \beta$ and b cell parameters increase regularly when the temperature rises (Fig. 3). The specific heat does not show any anomalous behaviour with temperature except for a very slight slope change near 260 K. All these results show that there is no first- or second-order phase transition for CrDEC in the temperature range studied. The crystal structure was determined by X-ray diffraction on a single crystal, and despite the bad resolution resulting from the small size and partial decomposition of the crystal, some anomalies were observed. The abnormally long Cr–C(3) and abnormally short C(3)–O(3) distances could be a result of the poor quality of the experimental dataset, but they could also be explained by the fact that this group starts to be thermally unstable near the decomposition temperature. It is noteworthy that only the hydrogen atoms of the methyl groups could not be localized. This suggests that, above 250 K, the methyl groups start to rotate, and this is why they are not located precisely in the X-ray structure, and also why some neutron reflections, especially those to which the hydrogen atoms contribute the most, are affected by the increase in temperature. In order to check this hypothesis, the neutron structure factors were calculated when the hydrogen atoms of the methyl groups were allowed to rotate [23]. Three cases were considered: (i) hypothesis **H1** consisted of examining the rotation of the C(5)H(51)–H(52)H(53) methyl groups around the C(4)–C(5) axis and looking for any variation of the intensity of the $(\bar{1}2\ 0\ 0)$ reflection; (ii) hypothesis **H2** considers the existence of two conformers, C(5)H(51)H(52)H(53) and C(5)H(51)H(52)H(53), shifted with respect to each other by a $2\pi/6$ rotation, as was found in the methyl-

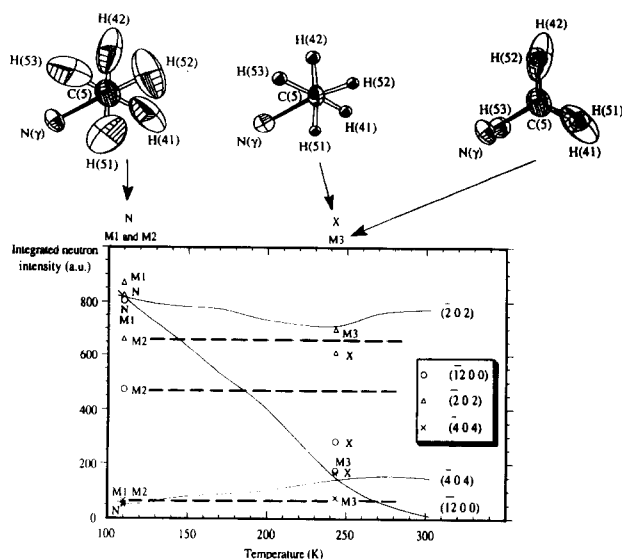


Fig. 6. Temperature-dependence of the observed and calculated neutron diffraction intensities for different models (X, N, M1 to M3).

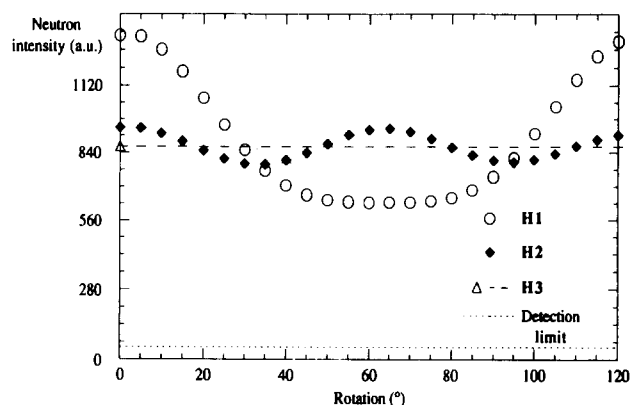


Fig. 7. Variation of $(\bar{1}2\ 0\ 0)$ intensity reflection vs. the rotation angle of methyl groups for the three hypotheses, **H1**, **H2** and **H3**.

carbynechromium complex as the temperature rose [25]; again a rotation of these two conformers around the C(4)–C(5) axis was considered; (iii) hypothesis **H3** consists of a continuous and dynamic movement of methyl groups.

To simplify the calculations on the rotation effect of the hydrogen atoms of the methyl groups, isotropic values for the hydrogen atoms were used. The influence of the anisotropic/isotropic thermal parameters of the hydrogen atoms on the intensity is negligible as can be seen in Fig. 6 for the points N and M1. For the three models, the $(\bar{1}2\ 0\ 0)$ neutron intensity was very sensitive to these rotations (Fig. 7), while most of the other reflections are practically unchanged. According to the **H3** hypothesis, there should be an obvious decrease in intensity if the rotation of the methyl groups is considered to be free. However, the calculated intensity remains high and is well above the detection limit. The **H2** hypothesis also gives an absolute lowering of the intensity and a modulation of this intensity as a function of the rotation of the methyl groups. The **H1** hypothesis gives the highest variation in intensity, starting from 1317 a.u. to reach 597 a.u. for a rotation of 60° . This value remains high when compared to the experimental error and so should be observable. Thus, none of the three hypotheses completely explains the experimental observations. A complementary calculation was done in order to take into account the intensity of the other two reflections $(\bar{2}\ 0\ 2)$ and $(\bar{4}\ 0\ 4)$. N and X (Table 4 and Fig. 6) are the calculated neutron intensities for the 110 K and 243 K experiments, respectively, using the results of the neutron and X-ray experiments. When a rotation of 60° is applied to the hydrogen atoms using neutron structure at 110 K, the $(\bar{1}2\ 0\ 0)$ intensity decreases, but it is still not enough to fit the neutron results at room temperature (model M2). When all the atomic positions as determined by X-ray diffraction at 243 K are used (model M3), the calculated intensity fits better the

Table 4
Experimental and structural models used in the modelling of the neutron intensity of CrDEC

Model	Positions and thermal parameters	Rotation
N	Neutron structure at 110 K [1]	
X	X-ray structure at 243 K [5]	
M1	Neutron structure at 110 K except for H(51) to H(53) atoms with isotropic thermal parameters.	
M2	Neutron structure at 110 K, except for H(51) to H(53) atoms with isotropic thermal parameters.	60°
M3	X-ray structure at 243 K, except for H(51) to H(53) positions as defined in the M2 model.	60°

experimental points. Therefore, with a simple rotation of the methyl group and an adjustment of the structural parameters of the other atoms using the parameters of the right temperature, it is possible to interpret the neutron intensity of the three reference reflections.

Despite our attempts to explain the experimental data with a model, it is difficult at present to explain the observed phenomena. There is surely an order-disorder in the motion of the hydrogen atoms of the methyl groups, but this is also a result of some deformation in the skeleton of the molecule and in particular of the carbonyl groups. More experimental work is needed here. In particular a complete neutron structure of the compound near room temperature would give an even greater understanding of the phenomenon.

4. Supplementary material

Thermal anisotropic parameters (U_{ij}) at 293 K have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

Authors wish to thank Dr. Marcus Braden of LLB for his help during the neutron diffraction experiment and M. Jacques Chevreul and Gilles Boëmare of the laboratoire CPS for their technical assistance. Part of the calculation was performed at the LLB on SUN and CONVEX and Marie-Noëlle Ohnet and Anne Spasojevic de Biré wish to thank the system team for their help.

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