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CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(3,3,4,4-TETRAMETHYL-3,4-DIHYDRODIAZETE)BIS(TRICARBONYLCHROMIUM), $(N_2C_2Me_4)_3[Cr(CO)_3]_2$

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Summary

Crystals of $C_{24}H_{36}N_6O_6Cr_2$ are monoclinic, *a* 15.380(3), *b* 13.965(2), *c* 14.459(3) Å, β 92.18(1)°; $Z = 4$; space group $P2_1$ with two independent molecules in the asymmetric unit. The crystal structure was determined from X-ray diffractometer data by direct methods and refined by least-squares methods to $R = 0.066$ for 2430 independent observed reflections. It consists of discrete molecules, in which each Cr atom is surrounded by three *cis* carbonyl groups and three *cis* nitrogen atoms of three 3,3,4,4-tetramethyl-1,2-diazetine ligands, in a deformed octahedral coordination. There is no evidence of intramolecular Cr · · · Cr interaction.

Introduction

There is much current interest in the field of transition-metal complexes of diazenes [1–4], and the preparations and properties of chromium and tungsten complexes of 3,3,4,4-tetramethyl-1,2-diazetine were recently described [5]; of these, the chromium complex $Cr_2(N_2C_2Me_4)_3(CO)_6$ proved to be particularly stable. It was deemed of interest to determine the interatomic distances and the bond angles in this compound, using X-ray diffraction methods on a single crystal, and to relate its structural features to those of other complexes. This paper describes the structure analysis carried out on the title compound.

Results and discussion

The crystal structure of the title compound involves discrete molecules. The interatomic distances and bond angles of the two independent molecules are listed in Table 1; the average values with their standard errors are given in Table 2. The representation of the molecules with the numbering scheme, drawn with the program ORTEP [7], is given in Fig. 1. Each Cr atom is octahedrally bonded to three carbon

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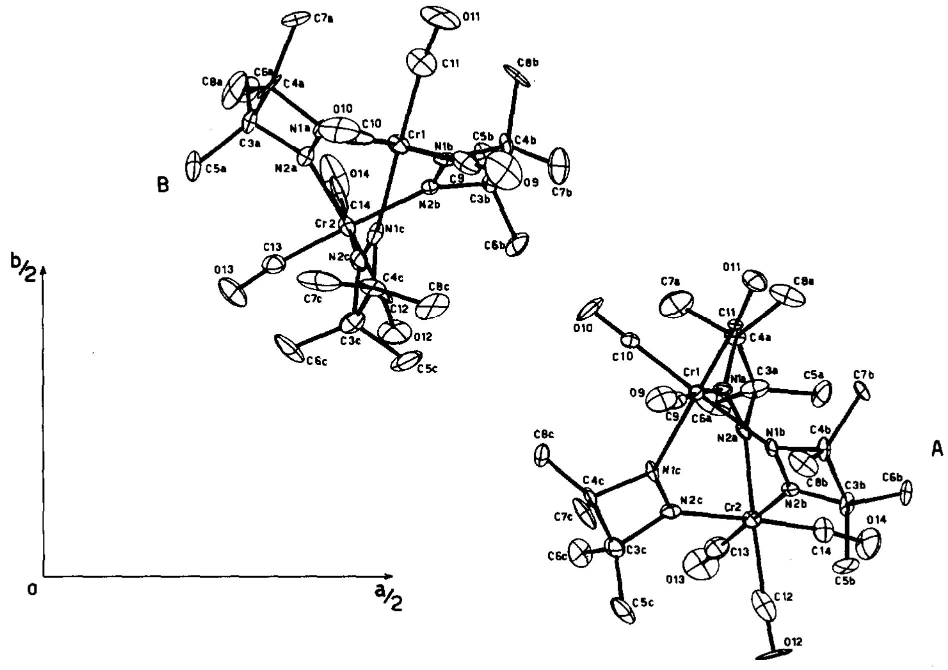

Fig. 1. ORTEP plot of the molecules, down *c* axis of cell. Thermal ellipsoids include 20% probability of electron density.

atoms of *cis* carbonyl groups and to three *cis* nitrogen atoms of three 3,3,4,4-tetramethyl-1,2-diazetine ligands. All the carbonyl groups are terminal.

The metal atoms have virtual C_{3v} symmetry and the whole molecule in each case has virtual D_{3h} symmetry, though it exhibits no real crystallographic symmetry and all the atoms occupy general positions. The IR spectrum [5] shows two carbonyl stretching bands, corresponding to the A_1 and E modes of the local C_{3v} symmetry for each *cis* $Cr(CO)_3$ unit.

The CO stretching and stretch–stretch interaction force constants calculated by Cotton-Kraihanzel's method [8] have values $k_1 = 14.05$ and $k_i = 0.23$ mdyn Å^{-1} respectively, suggesting a substantial π-acceptor capability for the azo group in the ligand, in agreement with the observation made on the similar Cr complex of 2,3-diazabicyclo[2,2,1]hept-2-ene [2]; the k_1 value for the title complex is indeed about 1.0 mdyn Å^{-1} larger than that of the Cr(dien)$(CO)_3$ complex [9], in which the nitrogen ligand has σ-bonding capability only. The Cr–N bond lengths (range 2.03–2.08 Å) are consequently shorter than those (2.185 Å) in Cr(dien)$(CO)_3$ [10], and comparable with those (2.056 Å) in $[Cr(sal\text{-}R\text{-}pn)_2]^+$ [11].

The Cr–C bond lengths (range 1.80–1.97 Å) on the other hand, are longer than those (1.816 Å) in Cr(dien)$(CO)_3$ [10] (which exhibits a stronger π-backbonding Cr → CO), but shorter than those (1.92 Å) in $Cr(CO)_6$ [12], and comparable with those (1.816 Å) in $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ [13]: this effect can be attributed to the diazetine ligand, which is a poorer π-acceptor than a CO group. The Cr–C–O angles are in the range 179–166°. The C–O bond lengths (range 1.10–1.19 Å) can be compared with the value 1.143 Å in $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ [13].

(Continued on p. 75)

TABLE 1

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

Molecule A			
Cr(1)···Cr(2)	3.831(3)		
In the coordination octahedra			
Cr(1)–N(1a)	2.03(1)	Cr(2)–N(2a)	2.03(1)
Cr(1)–N(1b)	2.07(1)	Cr(2)–N(2b)	2.05(1)
Cr(1)–N(1c)	2.08(1)	Cr(2)–N(2c)	2.04(1)
Cr(1)–C(9)	1.81(2)	Cr(2)–C(12)	1.97(2)
Cr(1)–C(10)	1.87(1)	Cr(2)–C(13)	1.89(2)
Cr(1)–C(11)	1.80(1)	Cr(2)–C(14)	1.83(2)
N(1a)–Cr(1)–N(1b)	83.9(4)	N(2a)–Cr(2)–N(2b)	83.3(4)
N(1a)–Cr(1)–N(1c)	85.3(4)	N(2a)–Cr(2)–N(2c)	86.0(4)
N(1b)–Cr(1)–N(1c)	84.6(4)	N(2b)–Cr(2)–N(2c)	86.8(4)
N(1a)–Cr(1)–C(9)	176.4(6)	N(2a)–Cr(2)–C(12)	177.7(6)
N(1a)–Cr(1)–C(10)	95.6(6)	N(2a)–Cr(2)–C(13)	96.9(6)
N(1a)–Cr(1)–C(11)	96.1(5)	N(2a)–Cr(2)–C(14)	96.0(6)
N(1b)–Cr(1)–C(9)	92.7(6)	N(2b)–Cr(2)–C(12)	96.1(5)
N(1b)–Cr(1)–C(10)	178.4(5)	N(2b)–Cr(2)–C(13)	179.8(6)
N(1b)–Cr(1)–C(11)	95.1(5)	N(2b)–Cr(2)–C(14)	96.2(6)
N(1c)–Cr(1)–C(9)	93.2(6)	N(2c)–Cr(2)–C(12)	96.2(6)
N(1c)–Cr(1)–C(10)	96.9(5)	N(2c)–Cr(2)–C(13)	93.3(6)
N(1c)–Cr(1)–C(11)	178.5(5)	N(2c)–Cr(2)–C(14)	176.6(6)
C(9)–Cr(1)–C(10)	87.8(7)	C(12)–Cr(2)–C(13)	83.7(7)
C(9)–Cr(1)–C(11)	85.3(7)	C(12)–Cr(2)–C(14)	81.9(7)
C(10)–Cr(1)–C(11)	83.4(6)	C(13)–Cr(2)–C(14)	83.7(7)
In the carbonyls			
C(9)–O(9)	1.16(2)	C(12)–O(12)	1.10(3)
C(10)–O(10)	1.13(2)	C(13)–O(13)	1.16(2)
C(11)–O(11)	1.14(2)	C(14)–O(14)	1.18(2)
Cr(1)–C(9)–O(9)	174(1)	Cr(2)–C(12)–O(12)	169(1)
Cr(1)–C(10)–O(10)	179(1)	Cr(2)–C(13)–O(13)	173(1)
Cr(1)–C(11)–O(11)	174(1)	Cr(2)–C(14)–O(14)	173(2)
In the 3,3,4,4-tetramethyl-3,4-dihydrodiazete ligands			
N(1a)–N(2a)	1.28(2)	C(3b)–C(5b)	1.48(2)
N(1a)–C(4a)	1.53(2)	C(3b)–C(6b)	1.58(2)
N(2a)–C(3a)	1.58(2)	C(4b)–C(7b)	1.55(2)
C(3a)–C(4a)	1.59(2)	C(4b)–C(8b)	1.47(2)
C(3a)–C(5a)	1.52(2)	N(1c)–N(2c)	1.26(2)
C(3a)–C(6a)	1.48(2)	N(1c)–C(4c)	1.50(2)
C(4a)–C(7a)	1.52(3)	N(2c)–C(3c)	1.48(2)
C(4a)–C(8a)	1.55(2)	C(3c)–C(4c)	1.56(2)
N(1b)–N(2b)	1.26(2)	C(3c)–C(5c)	1.55(2)
N(1b)–C(4b)	1.52(2)	C(3c)–C(6c)	1.54(2)
N(2b)–C(3b)	1.52(2)	C(4c)–C(7c)	1.55(2)
C(3b)–C(4b)	1.61(2)	C(4c)–C(8c)	1.52(2)
Cr(1)–N(1a)–N(2a)	128.5(9)	N(1b)–C(4b)–C(8b)	112(1)
Cr(1)–N(1a)–C(4a)	134.4(8)	C(3b)–C(4b)–C(7b)	116(1)
Cr(2)–N(2a)–N(1a)	129.3(9)	C(3b)–C(4b)–C(8b)	117(1)
Cr(2)–N(2a)–C(3a)	135.9(9)	C(7b)–C(4b)–C(8b)	114(1)
N(1a)–N(2a)–C(3a)	95(1)	N(2b)–C(3b)–C(5b)	114(1)

TABLE 1 (continued)

Molecule A

N(2a)–N(1a)–C(4a)	96(1)	N(2b)–C(3b)–C(6b)	109(1)
N(1a)–C(4a)–C(3a)	85(1)	C(4b)–C(3b)–C(5b)	117(1)
N(2a)–C(3a)–C(4a)	83.0(9)	C(4b)–C(3b)–C(6b)	116(1)
N(1a)–C(4a)–C(7a)	111(1)	C(5b)–C(3b)–C(6b)	113(1)
N(1a)–C(4a)–C(8a)	112(1)	Cr(1)–N(1c)–N(2c)	128.1(8)
C(3a)–C(4a)–C(7a)	115(1)	Cr(1)–N(1c)–C(4c)	134.8(8)
C(3a)–C(4a)–C(8a)	115(1)	Cr(2)–N(2c)–N(1c)	129.1(8)
C(7a)–C(4a)–C(8a)	115(1)	Cr(2)–N(2c)–C(3c)	136.5(9)
N(2a)–C(3a)–C(5a)	108(1)	N(1c)–N(2c)–C(3c)	94(1)
N(2a)–C(3a)–C(6a)	111(1)	N(2c)–N(1c)–C(4c)	97(1)
C(4a)–C(3a)–C(5a)	119(1)	N(1c)–C(4c)–C(3c)	82.4(9)
C(4a)–C(3a)–C(6a)	117(1)	N(2c)–C(3c)–C(4c)	86(1)
C(5a)–C(3a)–C(6a)	113(1)	N(1c)–C(4c)–C(7c)	110(1)
Cr(1)–N(1b)–N(2b)	129.4(8)	N(1c)–C(4c)–C(8c)	110(1)
Cr(1)–N(1b)–C(4b)	133.4(9)	C(3c)–C(4c)–C(7c)	117(1)
Cr(2)–N(2b)–N(1b)	127.8(8)	C(3c)–C(4c)–C(8c)	117(1)
Cr(2)–N(2b)–C(3b)	136.2(8)	C(7c)–C(4c)–C(8c)	116(1)
N(1b)–N(2b)–C(3b)	95.9(9)	N(2c)–C(3c)–C(5c)	115(1)
N(2b)–N(1b)–C(4b)	97.1(9)	N(2c)–C(3c)–C(6c)	113(1)
N(1b)–C(4b)–C(3b)	83.3(9)	C(4c)–C(3c)–C(5c)	117(1)
N(2b)–C(3b)–C(4b)	83.7(9)	C(4c)–C(3c)–C(6c)	116(1)
N(1b)–C(4b)–C(7b)	110(1)	C(5c)–C(3c)–C(6c)	109(1)

Molecule B

Cr(1) · · · Cr(2)	3.830(3)		

In the coordination octahedra

Cr(1)–N(1a)	2.04(1)	Cr(2)–N(2a)	2.06(1)
Cr(1)–N(1b)	2.05(1)	Cr(2)–N(2b)	2.07(1)
Cr(1)–N(1c)	2.07(1)	Cr(2)–N(2c)	2.07(1)
Cr(1)–C(9)	1.90(2)	Cr(2)–C(12)	1.87(2)
Cr(1)–C(10)	1.88(2)	Cr(2)–C(13)	1.86(2)
Cr(1)–C(11)	1.89(2)	Cr(2)–C(14)	1.84(2)
N(1a)–Cr(1)–N(1b)	88.3(5)	N(2a)–Cr(2)–N(2b)	87.7(4)
N(1a)–Cr(1)–N(1c)	85.2(5)	N(2a)–Cr(2)–N(2c)	84.0(5)
N(1b)–Cr(1)–N(1c)	84.2(5)	N(2b)–Cr(2)–N(2c)	81.9(5)
N(1a)–Cr(1)–C(9)	176.8(7)	N(2a)–Cr(2)–C(12)	176.8(7)
N(1a)–Cr(1)–C(10)	92.9(8)	N(2a)–Cr(2)–C(13)	93.3(6)
N(1a)–Cr(1)–C(11)	95.4(7)	N(2a)–Cr(2)–C(14)	95.5(8)
N(1b)–Cr(1)–C(9)	93.3(7)	N(2b)–Cr(2)–C(12)	95.5(7)
N(1b)–Cr(1)–C(10)	175.8(6)	N(2b)–Cr(2)–C(13)	178.0(6)
N(1b)–Cr(1)–C(11)	95.1(6)	N(2b)–Cr(2)–C(14)	96.3(6)
N(1c)–Cr(1)–C(9)	92.1(6)	N(2c)–Cr(2)–C(12)	96.4(7)
N(1c)–Cr(1)–C(10)	91.9(6)	N(2c)–Cr(2)–C(13)	96.4(6)
N(1c)–Cr(1)–C(11)	179.1(7)	N(2c)–Cr(2)–C(14)	178.1(7)
C(9)–Cr(1)–C(10)	85.4(9)	C(12)–Cr(2)–C(13)	83.6(8)
C(9)–Cr(1)–C(11)	87.3(8)	C(12)–Cr(2)–C(14)	84.1(9)
C(10)–Cr(1)–C(11)	88.8(8)	C(13)–Cr(2)–C(14)	85.4(7)

In the carbonyls

C(9)–O(9)	1.14(2)	C(12)–O(12)	1.15(2)
C(10)–O(10)	1.15(2)	C(13)–O(13)	1.14(2)
C(11)–O(11)	1.11(3)	C(14)–O(14)	1.18(2)

TABLE 1 (continued)

Molecule B			
Cr(1)–C(9)–O(9)	171(2)	Cr(2)–C(12)–O(12)	173(2)
Cr(1)–C(10)–O(10)	167(2)	Cr(2)–C(13)–O(13)	171(1)
Cr(1)–C(11)–O(11)	168(2)	Cr(2)–C(14)–O(14)	177(2)
In the 3,3,4,4-tetramethyl-3,4-dihydrodiazete ligands			
N(1a)–N(2a)	1.28(2)	C(3b)–C(5b)	1.50(2)
N(1a)–C(4a)	1.50(2)	C(3b)–C(6b)	1.50(2)
N(2a)–C(3a)	1.47(2)	C(4b)–C(7b)	1.56(2)
C(3a)–C(4a)	1.49(3)	C(4b)–C(8b)	1.55(2)
C(3a)–C(5a)	1.62(3)	N(1c)–N(2c)	1.29(2)
C(3a)–C(6a)	1.58(3)	N(1c)–C(4c)	1.49(2)
C(4a)–C(7a)	1.64(3)	N(2c)–C(3c)	1.51(2)
C(4a)–C(8a)	1.50(3)	C(3c)–C(4c)	1.64(3)
N(1b)–N(2b)	1.23(2)	C(3c)–C(5c)	1.53(3)
N(1b)–C(4b)	1.48(2)	C(3c)–C(6c)	1.52(3)
N(2b)–C(3b)	1.52(2)	C(4c)–C(7c)	1.55(3)
C(3b)–C(4b)	1.50(2)	C(4c)–C(8c)	1.51(3)
Cr(1)–N(1a)–N(2a)	127.7(9)	N(1b)–C(4b)–C(8b)	113(1)
Cr(1)–N(1a)–C(4a)	139(1)	C(3b)–C(4b)–C(7b)	119(1)
Cr(2)–N(2a)–N(1a)	129.3(9)	C(3b)–C(4b)–C(8b)	120(1)
Cr(2)–N(2a)–C(3a)	136(1)	C(7b)–C(4b)–C(8b)	105(1)
N(1a)–N(2a)–C(3a)	95(1)	N(2b)–C(3b)–C(5b)	115(1)
N(2a)–N(1a)–C(4a)	93(1)	N(2b)–C(3b)–C(6b)	109(1)
N(1a)–C(4a)–C(3a)	85(1)	C(4b)–C(3b)–C(5b)	120(1)
N(2a)–C(3a)–C(4a)	86(1)	C(4b)–C(3b)–C(6b)	118(1)
N(1a)–C(4a)–C(7a)	106(1)	C(5b)–C(3b)–C(6b)	110(1)
N(1a)–C(4a)–C(8a)	112(2)	Cr(1)–N(1c)–N(2c)	127(1)
C(3a)–C(4a)–C(7a)	115(2)	Cr(1)–N(1c)–C(4c)	138(1)
C(3a)–C(4a)–C(8a)	122(2)	Cr(2)–N(2c)–N(1c)	129(1)
C(7a)–C(4a)–C(8a)	113(2)	Cr(2)–N(2c)–C(3c)	132(1)
N(2a)–C(3a)–C(5a)	107(1)	N(1c)–N(2c)–C(3c)	98(1)
N(2a)–C(3a)–C(6a)	112(1)	N(2c)–N(1c)–C(4c)	95(1)
C(4a)–C(3a)–C(5a)	116(2)	N(1c)–C(4c)–C(3c)	85(1)
C(4a)–C(3a)–C(6a)	121(2)	N(2c)–C(3c)–C(4c)	81(1)
C(5a)–C(3a)–C(6a)	110(2)	N(1c)–C(4c)–C(7c)	110(1)
Cr(1)–N(1b)–N(2b)	128.5(9)	N(1c)–C(4c)–C(8c)	116(1)
Cr(1)–N(1b)–C(4b)	138.9(9)	C(3c)–C(4c)–C(7c)	113(1)
Cr(2)–N(2b)–N(1b)	129.8(9)	C(3c)–C(4c)–C(8c)	116(2)
Cr(2)–N(2b)–C(3b)	132.9(9)	C(7c)–C(4c)–C(8c)	114(2)
N(1b)–N(2b)–C(3b)	97(1)	N(2c)–C(3c)–C(5c)	110(1)
N(2b)–N(1b)–C(4b)	93(1)	N(2c)–C(3c)–C(6c)	114(1)
N(1b)–C(4b)–C(3b)	88(1)	C(4c)–C(3c)–C(5c)	107(1)
N(2b)–C(3b)–C(4b)	81.4(9)	C(4c)–C(3c)–C(6c)	120(1)
N(1b)–C(4b)–C(7b)	111(1)	C(5c)–C(3c)–C(6c)	119(2)

There is no evidence of Cr ··· Cr interaction, in agreement with the observed separation of the two $Cr(CO)_3$ units: the relevant distance is 3.831 Å. The bond lengths and angles in the ligand are comparable with those previously found [4,14,15]. The N–N bonds (range 1.23–1.29 Å) are longer than a double bond, owing to the σ-donation of the lone-pairs from nitrogen to chromium. The least-squares

TABLE 2

AVERAGE BOND DISTANCES (Å) AND ANGLES (°) WITH THEIR STANDARD ERRORS [a]

	N	x_m	σ_m	σ'_m
Cr···Cr	2	3.8306	0.0002	0.0021
Cr–N	12	2.053	0.005	0.003
Cr–C	12	1.857	0.013	0.005
C–O	12	1.147	0.007	0.006
N–N	6	1.265	0.008	0.007
N–C	12	1.510	0.009	0.005
C–C	6	1.567	0.022	0.009
$C–CH_3$	24	1.533	0.008	0.005
N–Cr–N	12	85.1	0.5	0.1
$N–Cr–C_{cis}$	24	95.0	0.3	0.1
$N–Cr–C_{trans}$	12	177.7	0.3	0.2
C–Cr–C	12	85.0	0.6	0.2
Cr–C–O	12	172.7	1.0	0.4
Cr–N–N	12	128.6	0.2	0.3
Cr–N–C	12	135.5	0.6	0.3
N–N–C	12	95.7	0.5	0.3
N–C–C	12	84.1	0.6	0.3
$N–C–CH_3$	24	111.3	0.5	0.2
$C–C–CH_3$	24	116.8	0.6	0.3
$CH_3–C–CH_3$	12	112.4	1.0	0.4

[a] All values were calculated with the formulae taken from ref. [6]:

$$x_m = \sum_{i=1}^{N} (x_i/\sigma_i^2) / \sum_{i=1}^{N} (1/\sigma_i^2)$$

$$\sigma_m = \left(\sum_{i=1}^{N} \left((x_i - x_m)^2/\sigma_i^2\right)/(N-1) \sum_{i=1}^{N} (1/\sigma_i^2) \right)^{1/2}$$

$$\sigma'_m = \left(\sum_{i=1}^{N} 1/\sigma_i^2 \right)^{-1/2}$$

planes of the ligands rings, the displacements of atoms from them, the $\Sigma(d/\sigma_\perp)^2$ values distributed like χ^2 ($n = 1$) with the corresponding probability P that the rings are non-planar and the dihedral angles are given in Table 3.

The packing of the molecules in the crystal is determinated by normal Van der Waals approaches. The shortest intermolecular distances are given in Table 4.

The low packing coefficient k of the structure [16], 0.65, can be attributed to the presence of numerous methyl groups.

Experimental

The $(N_2C_2Me_4)_3[Cr(CO)_3]_2$ complex was prepared by treating $Cr(CO)_6$ with 3,3,4,4-tetramethyl-1,2-diazetine-*N*-oxide in 3/2 ratio in n-heptane under argon and refluxing the solution for 22 h. After evaporation of the solvent and crystallization of the residue from toluene/petroleum ether, dark green crystals suitable for a single crystal X-ray diffractometric analysis, were obtained [5]. Solutions of the crystals have an intense red-violet colour.

TABLE 3

PLANARITY OF MOLECULAR FRAGMENTS

Plane	Equation [a], χ^2, P	Atoms [b]	Displacements
Aa	$-0.9319\ X'-0.1268\ Y-0.3398\ Z'+15.5911=0$	N(1a)*	0.026(10)
		N(2a)*	−0.026(10)
	$\chi^2=28.76$	C(3a)*	0.046(16)
	$P>99.0\%$	C(4a)*	−0.038(14)
		Cr(1)	−0.076(2)
		Cr(2)	−0.071(2)
Ab	$0.5284\ X'+0.6481\ Y-0.5484\ Z'-7.2955=0$	N(1b)*	−0.011(11)
		N(2b)*	0.009(10)
	$\chi^2=4.13$	C(3b)*	−0.016(15)
	$P=95.6\%$	C(4b)*	0.015(14)
		Cr(1)	0.033(2)
		Cr(2)	0.082(2)
Ac	$-0.3735\ X'+0.5046\ Y-0.7784\ Z'+7.4785=0$	N(1c)*	−0.003(10)
		N(2c)*	0.003(11)
	$\chi^2=0.43$	C(3c)*	−0.005(15)
	$P=48.1\%$	C(4c)*	0.005(14)
		Cr(1)	0.080(2)
		Cr(2)	−0.032(2)
Ba	$0.5088\ X'+0.6444\ Y-0.5709\ Z'-7.6364=0$	N(1a)*	−0.002(13)
		N(2a)*	0.002(12)
	$\chi^2=0.20$	C(3a)*	−0.005(20)
	$P=33.2\%$	C(4a)*	0.005(20)
		Cr(1)	−0.048(2)
		Cr(2)	−0.003(2)
Bb	$-0.3412\ X'+0.8294\ Y-0.4422\ Z'-3.4609=0$	N(1b)*	−0.025(11)
		N(2b)*	0.023(11)
	$\chi^2=19.22$	C(3b)*	−0.026(13)
	$P>99.0\%$	C(4b)*	0.038(16)
		Cr(1)	−0.155(3)
		Cr(2)	0.109(2)
Bc	$0.9586\ X'-0.1945\ Y-0.2079\ Z'-4.5941=0$	N(1c)*	0.004(10)
		N(2c)*	−0.005(11)
	$\chi^2=0.90$	C(3c)*	0.009(17)
	$P=64.5\%$	C(4c)*	−0.010(18)
		Cr(1)	0.086(2)
		Cr(2)	0.012(2)

Dihedral angles (°)					
Aa/Ab	112.9	Aa/Ac	123.3	Ab/Ac	123.8
Ba/Bb	127.8	Ba/Bc	118.8	Bb/Bc	113.4

[a] Transformation matrix from monoclinic X, Y, Z to orthogonal X', Y, Z' coordinates:

$$\begin{pmatrix} 1 & 0 & -\cos\beta^{\star} \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta^{\star} \end{pmatrix}.$$

[b] The atoms denoted by * were included in the calculation of the plane.

TABLE 4

SHORTEST INTERMOLECULAR APPROACHES (Å)

C(4a)A ··· O(13)A (i)	3.48	C(6c)A ··· O(14)B (iv)	3.39
C(5a)A ··· O(13)B (ii)	3.37	O(9)A ··· O(12)A (v)	3.28
C(8a)A ··· O(13)A (i)	3.29	O(9)A ··· C(8a)B (vi)	3.39
C(3b)A ··· O(9)B (iii)	3.50	O(13)A ··· O(13)B (iv)	3.49
C(5b)A ··· O(9)A (iii)	3.42	O(14)A ··· C(6b)B (vii)	3.34
C(6b)A ··· O(9)B (iii)	3.49	C(7c)B ··· O(11)B (vi)	3.42
C(7b)A ··· O(9)B (iii)	3.36	C(8c)B ··· O(10)B (vi)	3.31
C(8b)A ··· O(9)B (iii)	3.46		

Symmetry code

(i)	$2-x$	$1/2+y$	$-z$
(ii)	$1+x$	y	z
(iii)	$2-x$	$-1/2+y$	$1-z$
(iv)	$1-x$	$-1/2+y$	$-z$
(v)	$2-x$	$1/2+y$	$1-z$
(vi)	$1-x$	$-1/2+y$	$1-z$
(vii)	$2-x$	$-1/2+y$	$-z$

Data collection

A prismatic crystal of the title compound having approximate dimensions 0.32 × 0.30 × 0.34 mm was used for data collection. Accurate unit-cell dimensions were determined by a least-squares procedure of 2ϑ values for 25 reflections measured on a single-crystal Philips PW 1100 computer controlled diffractometer (using the graphite monochromated Mo-K_α radiation) of Centro di Studio per la Cristallografia strutturale del C.N.R., Pavia, Italy. The intensities of 4596 independent reflections were collected within the angular range $2 \leqslant \vartheta \leqslant 23°$, using the $\omega/2\vartheta$ scan technique with a constant speed of $0.050°\ \mathrm{s}^{-1}$ in ω. Three standard reflections were monitored every 240 min and showed only random fluctuations of intensities with time. The intensities were corrected for Lorentz and polarization factors and for absorption according to North et al. [17] and treated by Wilson's method [18], to give an approximate absolute scale and a mean isotropic thermal factor. 2430 reflections having $I \geqslant 3\sigma(I)$ ($\sigma(I)$ based on counting statistics) were considered observed and used in the structure analysis.

Crystal data

$C_{24}H_{36}N_6O_6Cr_2$, mol. wt. 608.62; monoclinic, a 15.380(3), b 13.965(2), c 14.459(3) Å, β 92.18(1)°; V 3103.3 Å^3; $Z=4$, D_c 1.30 g cm^{-3}; $F(000)=1272$; λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 7.76 cm^{-1}.

Systematic absences $0k0$, $k \neq 2n$ defined the possible space groups $P2_1/m$ and $P2_1$. The absence of the vector set $(0y0)$ in the three-dimensional Patterson map is not consistent with space group $P2_1/m$, the statistical distribution of the normalized structure factors $|E|$ ($\langle E \rangle = 0.863$ $\langle E^2 - 1 \rangle = 0.748$ $\langle E^3 \rangle = 1.355$ $\langle E^4 \rangle = 2.090$) agrees with an acentric space group. The space group is therefore $P2_1$ and this choice was confirmed by the subsequent structure refinement.

TABLE 5

ATOMIC COORDINATES WITH e.s.d.'s IN PARENTHESES ($\times 10^4$)

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Cr(1)	9453(1)	2916	3644(1)	5201(1)	6898(2)	3153(1)
Cr(2)	10183(1)	885(2)	2069(1)	4384(1)	5583(2)	963(1)
N(1a)	9787(7)	2977(8)	2300(7)	4097(8)	7160(9)	2362(9)
N(1b)	10529(6)	2035(8)	3791(7)	5835(8)	6658(8)	1957(8)
N(1c)	8798(6)	1662(8)	3260(7)	4853(6)	5474(9)	3028(8)
N(2a)	10063(7)	2302(8)	1789(7)	3825(7)	6714(9)	1637(8)
N(2b)	10775(6)	1368(7)	3274(7)	5578(7)	6211(8)	1263(8)
N(2c)	9037(7)	1017(8)	2717(7)	4589(7)	5041(9)	2284(9)
C(3a)	10197(10)	2968(12)	919(9)	3024(10)	7282(14)	1510(17)
C(4a)	9940(9)	3793(10)	1616(9)	3331(12)	7823(14)	2351(15)
C(5a)	11142(10)	2877(15)	652(13)	2212(10)	6568(17)	1644(18)
C(6a)	9565(12)	2737(14)	150(12)	2949(11)	7776(14)	530(13)
C(7a)	9093(14)	4313(16)	1367(14)	3712(13)	8897(13)	2143(19)
C(8a)	10703(14)	4452(13)	1936(12)	2858(12)	7772(19)	3238(15)
C(3b)	11597(8)	1123(11)	3849(10)	6416(8)	6267(9)	738(9)
C(4b)	11296(8)	2001(12)	4482(9)	6684(8)	6881(12)	1554(9)
C(5b)	11587(11)	156(11)	4265(12)	6320(9)	6703(13)	−206(9)
C(6b)	12419(8)	1310(12)	3258(9)	6801(10)	5280(12)	675(12)
C(7b)	11842(8)	2933(11)	4419(11)	7454(11)	6543(18)	2211(12)
C(8b)	11033(10)	1776(13)	5420(9)	6830(10)	7970(13)	1414(11)
C(3c)	8232(9)	450(11)	2782(10)	4508(11)	4045(12)	2676(11)
C(4c)	7923(8)	1249(10)	3445(10)	4827(11)	4610(12)	3627(14)
C(5c)	8367(11)	−563(13)	3197(13)	5271(14)	3429(13)	2380(15)
C(6c)	7714(10)	362(13)	1855(10)	3596(13)	3633(15)	2590(16)
C(7c)	7871(10)	985(14)	4484(11)	4090(16)	4715(13)	4324(13)
C(8c)	7212(9)	1918(13)	3064(16)	5692(14)	4300(15)	4066(17)
C(9)	9197(9)	2793(11)	4846(12)	6192(12)	6597(13)	3917(13)
C(10)	8500(9)	3741(10)	3506(11)	4620(15)	7021(12)	4264(14)
C(11)	10019(8)	3991(9)	4007(10)	5537(13)	8194(16)	3261(11)
C(12)	10350(11)	−490(16)	2333(10)	4829(12)	4531(14)	339(15)
C(13)	9639(10)	435(13)	958(13)	3319(11)	4980(11)	718(11)
C(14)	11185(9)	710(13)	1445(11)	4232(9)	6094(17)	−205(13)
O(9)	9022(8)	2805(10)	5616(9)	6732(11)	6475(14)	4471(9)
O(10)	7927(8)	4245(9)	3416(10)	4420(10)	7135(9)	5013(9)
O(11)	10314(7)	4691(8)	4285(8)	5818(12)	8902(10)	3444(12)
O(12)	10486(10)	−1263(8)	2347(11)	5024(10)	3874(10)	−88(11)
O(13)	9386(9)	168(10)	234(8)	2725(8)	4534(10)	490(9)
O(14)	11801(7)	495(10)	1028(8)	4138(8)	6375(14)	−969(8)

Structure determination and refinement

The crystal asymmetric unit consists of two independent molecules. The structure was solved by direct methods, using 252 reflections ($|E| \geqslant 1.7$) with the program MULTAN-78 [19]. In the phase determination 2035 Σ_2 relationships were used and for the PSI (zero) figure of merit the phases of 50 reflections ($|E| < 0.05$) were taken into account. The *E*-map computed from the phase set with the best consistency (highest ABS FOM = 1.1965 and lowest RESID = 11.55) revealed correctly 4 top peaks, corresponding to the chromium atoms, and other 59 of the expected 72 minor

TABLE 6

THERMAL PARAMETERS WITH e.s.d.'s IN PARENTHESES ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule A						
Cr(1)	27(1)	31(1)	36(1)	6(1)	2(1)	−4(1)
Cr(2)	34(1)	36(1)	31(1)	−1(1)	4(1)	−8(1)
N(1a)	34(5)	19(6)	39(6)	−4(6)	−1(5)	10(6)
N(1b)	17(5)	39(7)	40(7)	−5(5)	17(5)	−4(6)
N(1c)	16(5)	53(8)	17(5)	−13(5)	−11(4)	−3(6)
N(2a)	23(5)	39(8)	30(7)	−13(5)	1(5)	−14(6)
N(2b)	32(5)	24(6)	25(6)	−1(5)	17(5)	6(5)
N(2c)	40(6)	26(7)	31(6)	0(5)	−6(5)	−11(6)
C(3a)	79(10)	43(9)	28(8)	12(9)	1(7)	20(9)
C(4a)	44(8)	35(8)	22(7)	−3(7)	−27(6)	5(7)
C(5a)	44(9)	90(14)	122(16)	25(10)	55(10)	60(14)
C(6a)	117(15)	78(14)	63(12)	−41(12)	−67(11)	27(11)
C(7a)	117(16)	93(17)	89(15)	31(14)	−10(13)	43(14)
C(8a)	124(15)	61(13)	47(11)	−38(12)	9(10)	−5(10)
C(3b)	18(6)	68(12)	53(9)	5(7)	−31(6)	−4(9)
C(4b)	16(6)	70(11)	34(8)	2(7)	−15(5)	2(9)
C(5b)	70(10)	28(9)	63(11)	12(8)	−7(9)	32(8)
C(6b)	13(6)	82(12)	44(9)	8(7)	−3(6)	−3(9)
C(7b)	23(6)	44(9)	95(12)	−18(7)	−10(7)	−17(11)
C(8b)	83(10)	86(14)	14(7)	−35(11)	−3(7)	2(9)
C(3c)	43(8)	48(10)	49(9)	−9(8)	19(7)	5(9)
C(4c)	18(6)	47(10)	53(9)	−16(6)	6(6)	−17(8)
C(5c)	55(10)	82(14)	88(13)	−40(10)	−9(9)	40(12)
C(6c)	53(9)	97(14)	36(9)	−9(10)	−32(7)	1(9)
C(7c)	54(9)	114(16)	54(10)	−58(10)	15(7)	1(11)
C(8c)	21(7)	64(13)	194(22)	6(8)	−6(10)	−30(15)
C(9)	46(8)	36(10)	58(10)	3(8)	−27(8)	−24(9)
C(10)	36(8)	28(9)	66(11)	−1(7)	8(7)	17(8)
C(11)	21(6)	12(7)	62(9)	−2(6)	−3(6)	−26(7)
C(12)	57(10)	126(19)	26(9)	−41(12)	17(7)	−37(11)
C(13)	61(10)	59(12)	81(13)	7(9)	20(10)	−28(11)
C(14)	41(8)	75(13)	70(11)	0(9)	7(8)	0(11)
O(9)	97(8)	84(10)	58(8)	11(8)	0(7)	−15(8)
O(10)	69(7)	67(9)	120(11)	54(7)	−1(7)	−10(8)
O(11)	62(7)	57(8)	97(9)	−17(6)	−17(6)	−20(8)
O(12)	132(11)	15(6)	144(13)	37(7)	−37(9)	−19(8)
O(13)	123(10)	124(12)	37(7)	−4(9)	−27(7)	−49(8)
O(14)	67(7)	120(11)	95(9)	20(8)	44(7)	−6(9)
Molecule B						
Cr(1)	47(1)	46(2)	36(1)	−10(1)	1(1)	−15(1)
Cr(2)	28(1)	52(2)	41(1)	−10(1)	2(1)	−6(1)
N(1a)	37(6)	40(9)	63(9)	15(6)	−4(6)	6(7)
N(1b)	58(7)	22(7)	27(6)	0(6)	−13(6)	2(6)
N(1c)	25(5)	67(9)	48(7)	14(6)	−13(5)	−48(8)
N(2a)	29(6)	46(8)	51(8)	7(6)	6(5)	−3(7)
N(2b)	28(5)	28(7)	41(7)	1(5)	−2(5)	23(6)
N(2c)	29(6)	58(9)	60(9)	−3(6)	17(6)	21(8)
C(3a)	21(8)	69(14)	147(19)	16(8)	6(10)	−2(14)
C(4a)	58(10)	61(13)	123(17)	55(11)	25(11)	−3(14)
C(5a)	23(8)	114(18)	217(25)	9(11)	22(12)	27(19)

TABLE 6 (continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(6a)	59(10)	83(15)	91(13)	18(11)	−14(9)	60(13)
C(7a)	82(14)	25(11)	201(26)	20(10)	8(15)	−2(14)
C(8a)	67(11)	169(24)	113(16)	55(15)	65(12)	19(18)
C(3b)	23(7)	39(9)	39(8)	−3(6)	21(6)	−6(7)
C(4b)	18(6)	70(11)	42(8)	−11(8)	14(6)	−13(9)
C(5b)	46(8)	89(13)	20(8)	−23(9)	−3(6)	8(8)
C(6b)	53(9)	71(13)	72(12)	29(9)	27(9)	−9(10)
C(7b)	43(9)	164(22)	62(12)	4(12)	−19(8)	−1(14)
C(8b)	65(10)	57(11)	69(11)	−54(10)	4(8)	2(10)
C(3c)	62(10)	63(12)	45(10)	19(9)	4(8)	12(9)
C(4c)	74(11)	36(10)	111(16)	−11(9)	29(11)	54(11)
C(5c)	102(14)	49(11)	138(19)	40(11)	48(14)	18(12)
C(6c)	88(14)	93(17)	134(19)	−68(13)	5(13)	27(15)
C(7c)	195(22)	50(13)	79(14)	−26(14)	90(15)	2(11)
C(8c)	108(15)	81(16)	170(22)	39(13)	−99(15)	36(16)
C(9)	78(12)	68(13)	62(12)	−31(11)	10(10)	−15(11)
C(10)	141(17)	28(10)	69(13)	−14(11)	−1(12)	−25(10)
C(11)	89(13)	99(19)	39(10)	−18(13)	20(9)	−28(12)
C(12)	63(11)	62(13)	112(16)	−52(10)	14(11)	−35(13)
C(13)	54(9)	43(10)	58(10)	3(8)	0(8)	−12(9)
C(14)	29(8)	169(22)	67(12)	−53(11)	−3(8)	−22(15)
O(9)	134(12)	189(17)	74(10)	−38(13)	−64(9)	4(11)
O(10)	175(13)	78(10)	59(8)	−8(9)	65(9)	−36(8)
O(11)	156(14)	64(10)	144(15)	−48(10)	5(11)	−71(10)
O(12)	116(10)	71(10)	110(11)	1(8)	35(8)	−59(9)
O(13)	75(8)	107(11)	110(11)	−51(8)	−27(8)	−27(9)
O(14)	79(8)	257(21)	39(7)	−67(11)	−16(6)	35(10)

[a] The anisotropic parameters are of the form: $\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$.

peaks, corresponding to O, N and C atoms. The positions of the four unique chromium atoms were confirmed by the three-dimensional Patterson map. A subsequent three-dimensional difference Fourier revealed all the remaining 13 non-hydrogen atoms in the molecules.

A structure factor calculation based on the coordinates of all the 76 non-hydrogen atoms gave $R = 0.182$. Three cycles of least-squares refinement including scale factor and individual isotropic thermal parameters reduced the R index to 0.082. After several other refinement cycles with individual anisotropic thermal parameters, the R index dropped to 0.066; due to the large number of variables (685) this refinement had to be carried out in alternating cycles. Because of limitations on computer storage the 72 hydrogen atoms were disregarded: a final difference Fourier map showed no significant features other than possible positions of hydrogen atoms. At all stages of the structure analysis, the observed reflections were given unit weights, since the use of weights $\sigma^{-2}(|F_o|)$ led to the same results but also to some nonpositive-definite thermal factors.

Scattering factors for neutral atoms were taken from standard tables [20] and corrected for anomalous dispersion. The enantiomorphic structure was checked by reversing the sign of the y-coordinates of all atoms and a final R value of 0.122 was thereby obtained, indicating that the original model was correct.

The positional and thermal parameters are listed in Tables 5 and 6. A list of structure factors is available from the author on request.

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