Structure of Tricarbonyl[5-ethyl-2-(5'-ethyl-1',2',3',6'-tetrahydro-1'-methyl-2'-pyridyl)-1,6-dihydro-1-methylpyridine]chromium

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Abstract

The title compound, [$Cr(C_{16}H_{26}N_2)(CO)_3$], has been characterized as a structural isomer of compound (I) reported in the preceding paper [Trotter & Mak (1980). *Acta Cryst.* B36, 551–556]. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 19.226$ (2), $b = 10.567$ (2), $c = 9.457$ (1) Å, $Z = 4$. The structure and configuration were determined from Mo $K\alpha$ diffractometer data by direct methods and refined to R 0.028 for 1819 observed reflections. The dihydropyridine ring, in the form of an envelope, is bonded to the Cr atom in a pentahapto fashion *via* the six π electrons of its conjugated dienamine system, resulting in a distorted octahedral coordination. The tetrahydropyridine ring adopts a half-chair conformation, and the bond configuration around its N atom is distinctly pyramidal.

Introduction

In the preceding paper (Trotter & Mak, 1980), we reported the structural determination of two diastereomers, (I) and (II), of tricarbonyl[5-ethyl-2-(5'-ethyl-1',2',3',4'-tetrahydro-1'-methyl-2'-pyridyl)-1,6-dihydro-1-methylpyridine]chromium, which were ob-

tained by reacting tricarbonyl(3-ethyl-1,2-dihydro-1-methylpyridine)chromium (III) with methyllithium (Kutney, Mak, Mostowicz, Trotter & Worth, 1979). Interestingly, the reaction yielded a third isomeric product (IV) with virtually the same spectroscopic properties. In order to establish the structure of the title compound (IV) and its stereochemical correlation with (I) and (II), an X-ray crystallographic study has been undertaken.

Experimental

Crystals of complex (IV) are red plates elongated along **c** with (100) well developed. Unit-cell and space-group data were determined from precession photographs and diffractometer measurements.

Crystal data

(IV), $C_{19}H_{26}CrN_2O_3$, $M_r = 382.44$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 19.226$ (2), $b = 10.567$ (2), $c = 9.457$ (1) Å, $V = 1921.3$ Å^3, $D_c = 1.322$ Mg m^{-3} for $Z = 4$, μ(Mo $K\alpha$) = 0.634 mm^{-1}.

Intensity data were collected on a crystal with dimensions *ca* $0.1 \times 0.3 \times 0.4$ mm on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). A variable-speed ω–2θ scan over a range of $r = (0.85 + 0.35 \tan \theta)°$ in ω was used, and the scan was extended at both ends by $r/4$ for background measurement. Crystal orientation was monitored every 100 reflections. The intensities of three standard reflections, checked hourly throughout data collection, fluctuated within ±2%. Of the 2504 unique reflections measured up to $2\theta < 55°$, 1819 (72.6%) were considered observed at the $3\sigma(I)$ significance level, where $\sigma^2(I) = S + B + (0.04S)^2$, with $S =$ scan count and $B =$ normalized background count. Lorentz and polarization factors were applied to the raw data but no absorption correction was applied.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The most promising E map calculated with 481 assigned phases yielded peaks for 19 atoms in the molecule, and the remaining nonhydrogen atoms were located in successive cycles of struc-

(I)

(II)

(III)

(IV)
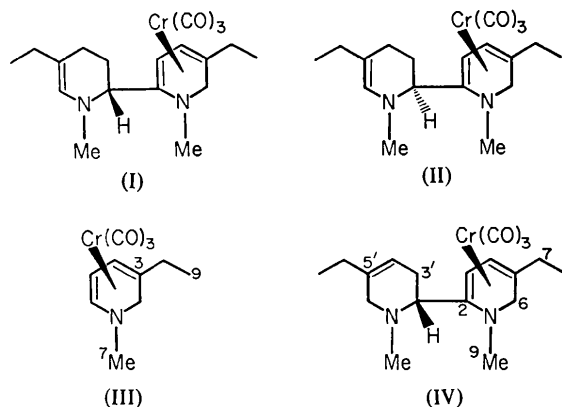
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Table 1. *Fractional coordinates* (Cr ×10⁵; C, N, *and* O ×10⁴; H × 10³) *with e.s.d.'s in parentheses*

	x	y	z
Cr	26318 (2)	26550 (4)	6695 (4)
N(1)	3567 (1)	3701 (2)	423 (3)
C(2)	3729 (1)	2595 (2)	1191 (3)
C(3)	3563 (1)	1451 (2)	535 (4)
C(4)	3224 (1)	1447 (2)	−817 (3)
C(5)	3149 (1)	2538 (3)	−1573 (3)
C(6)	3612 (2)	3626 (3)	−1136 (3)
C(7)	2799 (2)	2635 (3)	−3006 (3)
C(8)	2223 (2)	1701 (4)	−3239 (4)
C(9)	3731 (2)	4962 (2)	993 (3)
N(1')	4764 (1)	3260 (2)	2488 (3)
C(2')	4069 (1)	2696 (3)	2641 (3)
C(3')	4073 (2)	1471 (3)	3476 (3)
C(4')	4497 (2)	1626 (3)	4807 (3)
C(5')	4931 (1)	2579 (3)	5003 (3)
C(6')	5024 (2)	3581 (3)	3898 (4)
C(7')	5361 (2)	2765 (4)	6338 (4)
C(8')	5298 (2)	1771 (4)	7447 (4)
C(9')	5250 (2)	2455 (4)	1723 (4)
O(1)	1496 (1)	748 (3)	967 (4)
C(10)	1948 (2)	1465 (3)	815 (4)
O(2)	2223 (1)	3278 (3)	3630 (2)
C(11)	2394 (2)	3056 (3)	2479 (3)
O(3)	1591 (1)	4538 (2)	−364 (3)
C(12)	2000 (2)	3814 (3)	21 (3)
H(3)	367	63	101
H(4)	304	64	−123
H(6a)	344	442	−158
H(6b)	410	346	−144
H(7a)	316	249	−374
H(7b)	260	348	−309
H(8a)	203	181	−423
H(8b)	186	178	−253
H(8c)	243	80	−320
H(9a)	423	518	78
H(9b)	366	498	204
H(9c)	343	562	53
H(2')	378	333	321
H(3'a)	429	78	287
H(3'b)	359	120	372
H(4')	445	97	558
H(6'a)	553	379	384
H(6'b)	477	436	423
H(7'a)	519	356	684
H(7'b)	586	286	610
H(8'a)	482	164	776
H(8'b)	562	192	826
H(8'c)	546	91	698
H(9'a)	505	221	78
H(9'b)	534	165	228
H(9'c)	570	289	157

Table 2. *Molecular dimensions*

Cr—N(1)	2·123 (2) Å		C(10)—Cr—C(11)	84·7 (1)°
Cr—C(2)	2·168 (2)		C(10)—Cr—C(12)	90·5 (1)
Cr—C(3)	2·201 (3)		C(11)—Cr—C(12)	89·6 (1)
Cr—C(4)	2·214 (3)		Cr—C(10)—O(1)	176·2 (3)
Cr—C(5)	2·345 (3)		Cr—C(11)—O(2)	177·5 (3)
Cr—C(10)	1·825 (3)		Cr—C(12)—O(3)	178·4 (3)
Cr—C(11)	1·822 (3)		C(2)—N(1)—C(6)	117·1 (2)
Cr—C(12)	1·830 (3)		C(2)—N(1)—C(9)	120·9 (2)
O(1)—C(10)	1·160 (4)		C(6)—N(1)—C(9)	113·6 (2)
O(2)—C(11)	1·161 (4)		N(1)—C(2)—C(3)	116·0 (2)
O(3)—C(12)	1·156 (4)		N(1)—C(2)—C(2')	120·1 (2)
N(1)—C(2)	1·411 (3)		C(2')—C(2)—C(3)	124·0 (3)
N(1)—C(6)	1·479 (4)		C(2)—C(3)—C(4)	120·1 (2)
N(1)—C(9)	1·472 (3)		C(3)—C(4)—C(5)	120·8 (2)
C(2)—C(3)	1·396 (4)		C(4)—C(5)—C(6)	116·0 (2)
C(3)—C(4)	1·436 (5)		C(4)—C(5)—C(7)	124·9 (3)
C(4)—C(5)	1·364 (4)		C(6)—C(5)—C(7)	117·0 (3)
C(5)—C(6)	1·512 (4)		C(5)—C(7)—C(8)	114·5 (3)
C(5)—C(7)	1·516 (4)		N(1)—C(6)—C(5)	106·2 (2)
C(7)—C(8)	1·500 (5)		C(2')—N(1')—C(6')	108·3 (2)
C(2)—C(2')	1·523 (4)		C(2')—N(1')—C(9')	113·3 (2)
N(1')—C(2')	1·470 (3)		C(6')—N(1')—C(9')	111·6 (2)
N(1')—C(6')	1·464 (4)		N(1')—C(2')—C(3')	113·1 (2)
N(1')—C(9')	1·456 (4)		N(1')—C(2')—C(2)	109·2 (2)
C(2')—C(3')	1·517 (4)		C(2)—C(2')—C(3')	114·3 (2)
C(3')—C(4')	1·508 (4)		C(2')—C(3')—C(4')	110·1 (2)
C(4')—C(5')	1·320 (4)		C(3')—C(4')—C(5')	122·8 (3)
C(5')—C(6')	1·498 (4)		C(4')—C(5')—C(6')	121·1 (3)
C(5')—C(7')	1·522 (4)		C(4')—C(5')—C(7')	124·0 (3)
C(7')—C(8')	1·490 (6)		C(6')—C(5')—C(7')	115·0 (3)
			C(5')—C(7')—C(8')	116·6 (3)
			N(1')—C(6')—C(5')	115·5 (2)

Scattering factors for nonhydrogen atoms were generated from the coefficients of analytical approximations (Cromer & Mann, 1968), and those for a spherically bonded H atom were taken from Stewart, Davidson & Simpson (1965). Computations were performed on an Amdahl 470 system with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$.
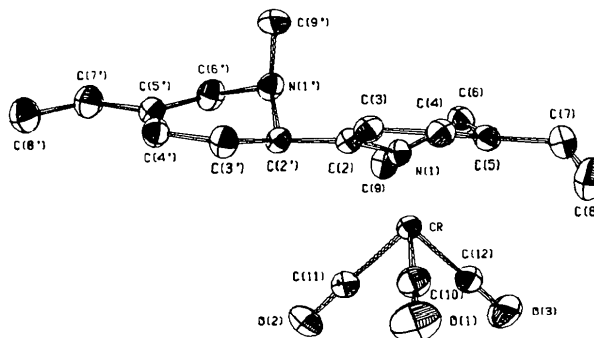
ture-factor and Fourier calculations. Continued full-matrix least-squares refinement with anisotropic thermal parameters followed by a difference map revealed all the H atoms, except two belonging to end methyl groups, which were then introduced at their calculated positions. Inclusion of the 26 H atoms with assigned isotropic thermal parameters in further least-squares cycles yielded, at convergence, $R = 0.028$ and weighted $R = 0.039$ for 1819 observed reflections.

Fig. 1. Atom numbering and drawing of (IV) viewed from the same perspective with respect to the Cr(CO)₃ group as for (I) and (II) in the preceding paper (Trotter & Mak, 1980). The thermal ellipsoids are drawn at the 40% probability level, and H atoms have been omitted for the sake of clarity.

Table 3. Torsion angles (°)

The sign convention is that defined by Klyne & Prelog (1960).

C(9)—N(1)—C(2)—C(3)	−178·7 (3)	C(6)—N(1)—C(2)—C(3)	−32·4 (3)	C(7')—C(5')—C(6')—N(1')	164·7 (3)
N(1)—C(2)—C(3)—C(4)	−2·3 (4)	C(6)—N(1)—C(2)—C(2')	147·3 (2)	C(4')—C(5')—C(6')—N(1')	−16·0 (4)
C(2)—C(3)—C(4)—C(5)	9·6 (4)	C(9)—N(1)—C(2)—C(2')	1·0 (3)	C(5')—C(6')—N(1')—C(9')	−79·9 (3)
C(3)—C(4)—C(5)—C(6)	17·3 (4)	N(1)—C(2)—C(2')—C(3')	167·5 (2)	C(5')—C(6')—N(1')—C(2')	45·6 (3)
C(3)—C(4)—C(5)—C(7)	−180·0 (3)	N(1)—C(2)—C(2')—N(1')	−64·7 (3)	C(6')—N(1')—C(2')—C(2)	168·9 (2)
C(4)—C(5)—C(6)—N(1)	−46·7 (3)	C(2)—C(2')—C(3')—C(4')	172·9 (2)	C(6')—N(1')—C(2')—C(3')	−62·6 (3)
C(4)—C(5)—C(7)—C(8)	31·3 (4)	C(2')—C(3')—C(4')—C(5')	−15·3 (4)	C(9')—N(1')—C(2')—C(2)	−66·7 (3)
C(8)—C(7)—C(5)—C(6)	−166·1 (3)	C(3')—C(4')—C(5')—C(6')	0·3 (5)	C(9')—N(1')—C(2')—C(3')	61·9 (3)
C(7)—C(5)—C(6)—N(1)	149·2 (2)	C(3')—C(4')—C(5')—C(7')	179·6 (3)	N(1')—C(2')—C(2)—C(3)	115·0 (3)
C(5)—C(6)—N(1)—C(9)	−155·9 (2)	C(4')—C(5')—C(7')—C(8')	2·3 (5)	N(1')—C(2')—C(3')—C(4')	47·1 (3)
C(5)—C(6)—N(1)—C(2)	55·4 (3)	C(8')—C(7')—C(5')—C(6')	−178·4 (3)		

Table 4. Least-squares planes and deviations (×10³ Å, σ ~ 0·003 Å) of selected atoms from the planes

Planes are defined in terms of Cartesian coordinates by
$$AX + BY + CZ = D.$$

(a) Plane 1 for C(2) − C(5) in the dihydropyridine ring

$$0·9123X − 0·0840Y − 0·4009Z = 5·8749$$

N(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(9)	C(2')
−108	−16	44	−39	19	569	−60	−149	21

(b) Plane 2 for C(4') − C(7') in the tetrahydropyridine ring

$$0·7415X − 0·5330Y − 0·4076Z = 3·6445$$

N(1')	C(2')	C(3')	C(4')	C(5')	C(6')	C(7')	C(9')	C(2)
352	−380	−6	−1	4	−1	−2	1794	−249

Numbering of the atoms in an ORTEP (Johnson, 1965) plot of the molecule is shown in Fig. 1, and the final positional parameters appear in Table 1.* Bond distances and angles are listed in Table 2, and torsion angles in the organic ligand in Table 3. Details of mean planes are given in Table 4.

Discussion

The present analysis showed that the title compound (IV) has the same stereochemical configuration as (I) (compare Fig. 1 with Fig. 1a of the preceding paper), the two structural isomers being differentiated by the disposition of the double bond in the tetrahydropyridine ring (see structural formulae). As in complexes (I) − (III), the dihydropyridine ring in (IV) is bonded to the Cr atom in a pentahapto fashion via the six π electrons of its dienamine system. The distances of the metal atom to the centres of the C(2)—C(3) and C(4)—C(5) double bonds are 2·069 (3) and 2·176 (3) Å, respec-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34801 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
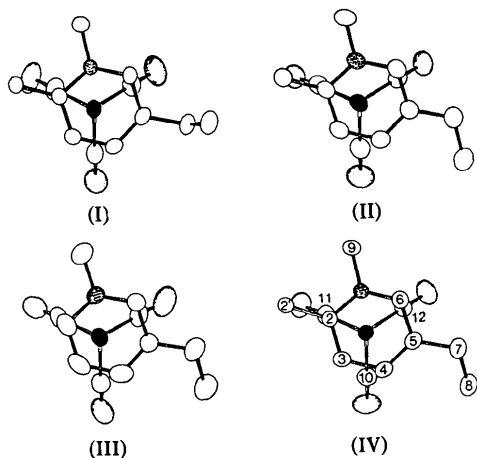
tively. The orientation of the Cr(CO)₃ group with respect to the dihydropyridine ligand is virtually identical in all four complexes (Fig. 2), clearly showing that the adopted conformation maximizes the overlap of the metal orbitals with the ligand π-orbitals in the resulting distorted octahedral coordination. This remarkable similarity in the series (I) − (IV) extends to the following aspects: (a) bond distances in the $Cr(CO)_3$ group; (b) bond-length variation in the dihydropyridine ring reflecting its dienamine character; (c) very nearly sp^2 hybridization for N(1); and (d) degree of puckering of the envelope-like dihydropyridine ring. Minor variations such as the spread in Cr—C—O and OC—Cr—CO bond angles and the orientation of the ethyl groups undoubtedly result from the different modes of molecular packing. Shifting of the double bond from the 5',6' position in (I) to the 4',5' position in (IV) leads to profound differences in the geometry of the tetrahydropyridine ring. In contrast to the conjugated enamine system present in (I), there is no appreciable interaction between the N(1') lone pair and the C(4')—C(5') double bond in (IV). The absence of π-electron delocalization in (IV) accounts for the following changes in ring geometry as compared with (I): (a) the bond configuration around N(1') is more pyramidal, and N(1')—C(6') is longer; (b) bond angles C(3')—C(4')—C(5') and C(4')—C(5')—C(7') are larger, while C(6')—C(5')—C(7') and N(1')—C(6')—C(5') are smaller; and (c) atom C(3') lies in the plane of the C(4') − C(7') fragment since C(4') becomes sp^2 hybridized, and as a result the tetrahydropyridine ring takes up a half-chair conformation similar to that of cyclohexene (Chiang & Bauer, 1969; Geise & Buys, 1970). In the pair of structural isomers (I) and (IV), the tetrahydropyridine ring stretches out from the (π-dihydropyridine)chromium tricarbonyl moiety. Inversion of the stereo configuration at C(2') brings the tetrahydropyridine ring to the proximity of the dihydropyridine ligand (see Fig. 1b of the preceding paper). In view of the dependence of tetrahydropyridine ring conformation on the location of the double bond, it is conceivable that steric effects overwhelmingly favour

Fig. 2. Comparison of the orientation of Cr(CO)$_3$ relative to the dihydropyridine ring in complexes (I) – (IV). The viewing direction is along the C_3 axis of the Cr(CO)$_3$ group. Note that the original paper on (III) (Bear & Trotter, 1973) employs a different numbering system and the opposite enantiomorph.

the formation of (II) over its hitherto unobserved structural isomer.

Unlike (I) and (II), each being a racemate, (IV) crystallizes in a noncentrosymmetric space group. The crystal lattice is built of molecules of the same chirality, with either the (2S,2'R) configuration (as depicted in the structural formula and in Fig. 1) or the enantiomeric (2R,2'S) configuration. This has been confirmed

by measuring the optical activity of individual single crystals.

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On the Absolute Configuration of the Tris(ethylenediamine)nickel(II) Cation.
I. The Structure and Absolute Configuration of (−)-[Ni(en)₃](NO₃)₂*

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Abstract

The X-ray crystal structure of [Ni(en)₃](NO₃)₂ has been redetermined in order to correlate the absolute configuration with the sign of the optical rotatory strength in the region of the Ni^{II} *d–d* transitions (*i.e.* 10 000 to 30 000 cm^{-1}). The space group is hexagonal, *P*6$_3$22, with $a = 8 \cdot 872$ (3), $c = 11 \cdot 359$ (3) Å, and $Z = 2$. The structure was refined by full-matrix least squares to a final *R* value of 0·022. The absolute configuration, determined by the Bijvoet method based on the anomalous dispersion of Ni, shows the [Ni(en)₃]$^{2+}$

* The symbol (−) preceding the chemical formula refers to the sign of *all* of the *d–d* transitions when measured with light normal to the *ab* plane of polished single-crystal plates.