

The Crystal Structure of Trigonal Tris(diphenyltriazine)cobalt(III)

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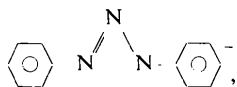
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The trigonal polymorph of tris(diphenyltriazine)cobalt(III) has a unit cell of space group $P\bar{3}$ with dimensions $a=b=17.559\pm 0.009$ and $c=18.546\pm 0.008$ Å. There are six molecules in the unit cell. The observed and calculated densities are 1.29 ± 0.02 and 1.30 g cm⁻³, respectively. The structure was refined by least-squares, using anisotropic temperature factors for the C and N atoms, to $R=0.078$ for 4197 integrated intensities measured with a diffractometer using Cu $K\alpha$ radiation. The refined structure confirms those features indicative of trigonal distortion which were reported by Corbett & Hoskins in their preliminary study of a monoclinic modification of the same compound. These distortions appear not to be unique to the diphenyltriazine complex, however, but may be typical of octahedral complexes formed from bidentate ligands having a short 'bite'. The molecules in the trigonal modification are not uniformly spaced along the z axis, and each unique diphenyltriazine moiety has a different molecular conformation. One phenyl ring has quite anisotropic thermal ellipsoids, which are probably indicative of partial disorder.

Introduction

The anion of diphenyltriazine,



acts as a bidentate ligand in forming a number of transition metal complexes. We will designate this anion by the abbreviation dpt. Corbett & Hoskins (1967) have given a preliminary report of a monoclinic form of the cobalt complex having in its unit cell two $\text{Co}(\text{dpt})_3$ moieties and two molecules of toluene. Their structure involves some unusual features. They reported an N–Co–N angle of 65° , which is significantly smaller than the 90° angle corresponding to octahedral symmetry, and therefore implies extreme trigonal distortion. Further, the structure of the dpt moiety was unusual in that the N–N–N bond angle is small, 105.0° , while the 20° tilt between the phenyl and NNN planes is comparatively large. The former angle is 116° in both the dimeric $\text{Cu}(\text{dpt})$ complex (Brown & Dunitz, 1961) and the tetrameric complex (O'Connor & Janusonis, 1968), 115.8° in $\text{Ni}_2(\text{dpt})_4$ (Corbett & Hoskins, 1968), 117° in $\text{Zn}_4\text{O}(\text{dpt})_2$ (Corbett & Hoskins, 1970), and the tilt angles were reported as 4° or less in the first two of these complexes. For neutral 4,4'-dibromodiphenyltriazine, Kondrashev (1962) reported a 113° bond angle at the apical nitrogen and a tilt of only 3° . It is also of interest that he found the two N–N bonds to be equivalent and shorter by nearly 0.09 Å than the 1.32 Å expected for an N–N bond of $\frac{3}{2}$ bond order. A refinement of the monoclinic $\text{Co}(\text{dpt})_3$ structure has not yet appeared.

Dr Richard Palmer of this laboratory has isolated $\text{Co}(\text{dpt})_3$ crystals which appear on microscopic examination to have trigonal or hexagonal symmetry, and which might therefore be advantageous for single-crystal polarized spectra studies. We have determined the structure of this form, both to facilitate interpretation of its crystal spectra and to verify the unique features of the $\text{Co}(\text{dpt})_3$ structure reported by Corbett & Hoskins.

Experimental

Opaque, purple $\text{Co}(\text{dpt})_3$ crystals were grown by interfacial crystallization using CH_3OH and CHCl_3 . Elemental analysis agreed well with that calculated from the formula, indicating no solvent of crystallization. Precession and Weissenberg photographs showed that the crystals are trigonal, and that there are no systematic absences. The unit-cell parameters were determined at 24°C by diffractometer examination of 12 orders along \mathbf{a} and \mathbf{b} , and 14 orders along \mathbf{c} . The d spacings were extrapolated to $\theta=90^\circ$ using the function $(\frac{1}{2})[\cos^2\theta/\sin\theta + (\cos^2\theta)/\theta]$. The values obtained using $\text{Cu } K\alpha=1.5405$ Å are $a=b=17.559\pm 0.009$ Å and $c=18.546\pm 0.008$ Å, where the error limits represent estimates based on the plot mentioned above. The measured density, 1.29 ± 0.02 g cm⁻³, agrees well with that calculated for six $\text{Co}(\text{dpt})_3$ molecules per unit cell, 1.30 g cm⁻³. Since $\text{Co}(\text{dpt})_3$ is likely to exist in two enantiomeric forms, the space group $P\bar{3}$ was tentatively assigned.

The crystal used for intensity measurements was a hexagonal prism 0.75 mm in length and having a maximum cross-sectional diameter of 0.25 mm. A data set of 4940 unique reflections within the sphere $2\theta < 128^\circ$ collected using a Picker FACS-1 system with incident beam monochromator. Integrated intensities were measured by the $\theta/2\theta$ scan technique using a scan rate

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Table 1. *Observed and calculated structure amplitudes and phase angles for tris(diphenyltriazine)cobalt(III)*

h	k	l	F_o	F_c	ϕ
0	0	0	100	100	0
0	0	1	100	100	0
0	0	2	100	100	0
0	0	3	100	100	0
0	0	4	100	100	0
0	0	5	100	100	0
0	0	6	100	100	0
0	0	7	100	100	0
0	0	8	100	100	0
0	0	9	100	100	0
0	0	10	100	100	0
0	0	11	100	100	0
0	0	12	100	100	0
0	0	13	100	100	0
0	0	14	100	100	0
0	0	15	100	100	0
0	0	16	100	100	0
0	0	17	100	100	0
0	1	0	100	100	0
0	1	1	100	100	0
0	1	2	100	100	0
0	1	3	100	100	0
0	1	4	100	100	0
0	1	5	100	100	0
0	1	6	100	100	0
0	1	7	100	100	0
0	1	8	100	100	0
0	1	9	100	100	0
0	1	10	100	100	0
0	1	11	100	100	0
0	1	12	100	100	0
0	1	13	100	100	0
0	1	14	100	100	0
0	1	15	100	100	0
0	1	16	100	100	0
0	1	17	100	100	0
0	2	0	100	100	0
0	2	1	100	100	0
0	2	2	100	100	0
0	2	3	100	100	0
0	2	4	100	100	0
0	2	5	100	100	0
0	2	6	100	100	0
0	2	7	100	100	0
0	2	8	100	100	0
0	2	9	100	100	0
0	2	10	100	100	0
0	2	11	100	100	0
0	2	12	100	100	0
0	2	13	100	100	0
0	2	14	100	100	0
0	2	15	100	100	0
0	2	16	100	100	0
0	2	17	100	100	0
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0	3	2	100	100	0
0	3	3	100	100	0
0	3	4	100	100	0
0	3	5	100	100	0
0	3	6	100	100	0
0	3	7	100	100	0
0	3	8	100	100	0
0	3	9	100	100	0
0	3	10	100	100	0
0	3	11	100	100	0
0	3	12	100	100	0
0	3	13	100	100	0
0	3	14	100	100	0
0	3	15	100	100	0
0	3	16	100	100	0
0	3	17	100	100	0
0	4	0	100	100	0
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0	4	2	100	100	0
0	4	3	100	100	0
0	4	4	100	100	0
0	4	5	100	100	0
0	4	6	100	100	0
0	4	7	100	100	0
0	4	8	100	100	0
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0	5	16	100	100	0
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0	8	7	100	100	0
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0	9	3	100	100	0
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0	10	12	100	100	0
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0	11	5	100	100	0
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0	12	6	100	100	0
0	12	7	100	100	0
0	12	8	100	100	0
0	12	9	100	100	0
0					

Table 1 (cont.)

Table with multiple columns and rows, containing dense text and data. The table is oriented vertically on the page. The columns are separated by vertical lines, and the rows are separated by horizontal lines. The text within the cells is small and dense, typical of a scientific or technical data table. The table appears to be a continuation of a larger table from a previous page, as indicated by the caption 'Table 1 (cont.)'. The data is organized into several distinct sections or groups, each with its own set of columns and headers. The overall layout is highly structured and detailed.

of $1^\circ/\text{minute}$ over a range of 1.6° plus an allowance for dispersion, and the background was counted for 20 sec at both extremes of the scan range. No adjustment of the crystal position was required during the course of data collection. Three reference reflections were monitored at approximately two hour intervals, and these showed a maximum variation of 2% during data collection. Standard deviations were calculated using the relation of Collins & Hoard (1970):

$$\sigma^2 = \left(\frac{1}{4}\right) (N + k^2 B) / (|F_o| Lp)^2 \quad (1)$$

where N is the total number of counts collected during the scan, k is the ratio of the scanning time to the sum of the background counting times, B is the total background count, and Lp is the Lorentz-polarization correction. Only the 4197 reflections for which $|F_o|$ exceeded the standard deviation were used in the structure determination and refinement, which gave $R = 0.078$. At the completion of the refinement F_c values were calculated for the 743 reflections treated as unobserved, and these were found to be small in every case. Inclusion of the small (but non-zero) structure amplitudes increased the final R index to 0.084. The linear absorption coefficient is 44.9 cm^{-1} . Transmission factors were measured for the 001 and 005 reflections, and these data were utilized to correct all the observed structure amplitudes for absorption using the approximate method of North, Phillips & Mathews (1968).

Structure analysis

A trial structure was deduced from the three-dimensional Patterson map. The largest non-origin vector, $0, 0, \frac{1}{2}$, suggested the cobalt ions were related by a translation of approximately $c/2$. From the five largest non-origin peaks and one additional vector, the cobalt ions could be assigned to the Wyckoff (c) and (d) positions, and the fractional z coordinates of the cobalt ions on the threefold axes at $x/a = -\frac{1}{3}, \frac{1}{3}$, and 0, which we designate by the letters A, B and C , could be estimated as 0.46, 0.04 and 0.25, respectively. The large magnitude of the Patterson vector $\frac{1}{3}, \frac{2}{3}, 0.43$ was the clue which led to a suitable trial structure. Its magnitude could be interpreted by assuming that pairs of molecules on the internal threefold axes (A and B) are at least approximately related by translation along this vector. This established the handedness of two of the three unique molecules, and reduced the number of light atom positions to be located. Additional investigation using triads of Patterson vectors produced a model consisting of two complete $\text{Co}(\text{dpt})_3$ molecules, and the third cobalt ion, which gave an R index of 0.51. The atomic scattering factors were taken from Cromer & Mann (1968) and *International Tables for X-ray Crystallography* (1962). An electron density map calculated using the phases deduced from this partial structure, and the 3452 structure amplitudes for which $\sin \theta/\lambda \leq 0.43$, revealed all of the non-hydrogen atoms with very little extraneous electron density. A second

structure factor calculation using the coordinates for all non-hydrogen atoms in the three unique molecules, and the same subset of reflections, reduced R to 0.31. Least-squares refinement using isotropic temperature factors and weights equal to $1/\sigma$ (where σ is the standard deviation based upon the counting statistics) converged to a relatively large R value, 0.175. The electron density map revealed that one ring composed of atoms C(1C)–C(6C) was badly distorted and the electron density profiles for the individual atoms were rather smeared out. Atoms C(1C)–C(5C) were therefore removed and a fine-grid electron density difference map was calculated in the region occupied by this ring using the complete set of 4197 structure factors phased on the remainder of the structure. Several possible disordered structures were tried, and the best of these was carried through four cycles of refinement, but the residual was not reduced by a statistically significant amount when account is taken of the additional parameters introduced (Hamilton, 1965). Since we were unable to represent the disorder using two discrete ring locations with adjustable occupancy factors, anisotropic temperature factors were introduced for these six carbon atoms which reduced R to 0.129 in two cycles. At this stage 25 of the 30 unique hydrogen atoms could be located in the electron density difference map as peaks exceeding four times the background. Isotropic temperature factors for these 25 atoms were permitted to vary in one cycle; these were averaged, and the isotropic temperature factor for these atoms was fixed at the average value, which gave $R = 0.122$. For subsequent cycles of refinement, weights were assigned using the relation $w = 2.109 - 0.0073|F_o| - 0.0004|F_o|^2$, where the coefficients were chosen to make the value of $\sum w(|F_o| - |F_c|)^2$ independent of $\sin \theta$. Further, the cobalt atoms were represented as zero-valent, and their scattering factors were modified to account for anomalous dispersion using values of $\Delta f'$ and $\Delta f''$ taken from *International Tables for X-ray Crystallography* (1962). Two cycles of full-matrix least-squares, using isotropic temperature factors for all atoms except C(1C)–C(6C), reduced R to 0.098. Three further cycles of refinement, using anisotropic temperature factors for all C and N atoms, produced the final R value, 0.078. In these final three cycles the number of variables exceeded the limitation of our least-squares

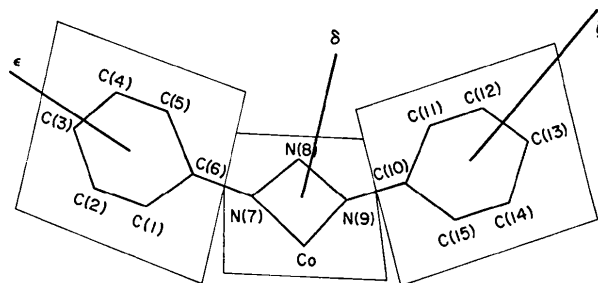


Fig. 1. Numbering of atoms and designations of the plane-normals in the diphenyltriazine moiety.

program, so each cycle was performed in four steps. In three of these the parameters for one cobalt and twelve carbon atoms were refined, and in the fourth the parameters for the three cobalt and six nitrogen atoms were varied. In the final cycle the shifts in all parameters were less than their standard deviations. The calculated and observed structure factors are compared in Table 1.

Description of the structure

Fig. 1 indicates the numbers used to designate the atoms in each of the three unique dpt moieties. Atomic

coordinates and thermal parameters appear in Table 2, while the bond distances and angles are given in Table 3. The present structure confirms two of the unusual features observed for the monoclinic form of $\text{Co}(\text{dpt})_3$ by Corbett & Hoskins (1967). Trigonal distortion is indicated by the N-Co-N angle of $64.8 \pm 0.3^\circ$ (in good agreement with their 65°), while the N-N-N bond angle of $103.2 \pm 0.5^\circ$ (they reported 105°) is considerably smaller than that found in other dpt complexes. The plane containing the three nitrogen atoms has its normal (δ in Fig. 1) tilted with respect to the (001) plane by 36.5° , in near agreement with the 37° expected for octahedral symmetry, so there is neither

Table 2. Atomic coordinates and temperature factors for tris(diphenyltriazine)cobalt(III)

Temperature factors in the form $\exp[-B(\sin \theta/\lambda)^2]$ or factors $\times 10^{-5}$ for the expression $\exp[-(b_{11}h^2 + 2b_{12}hk + \dots)]$. Hydrogen atoms assigned $B = 5.80$. Numbers in parentheses give the standard deviations in the last significant figures.

(a) Heavy atoms. Atomic coordinates are $\times 10^5$.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>					
				<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
Co(A)	-33333	33333	47834 (8)	3.566 (28)					
Co(B)	33333	-33333	4184 (7)	3.217 (26)					
Co(C)	0	0	26924 (8)	3.566 (28)					
C(1A)	-44957 (54)	47670 (39)	57394 (31)	666 (32)	560 (30)	255 (20)	427 (27)	-53 (19)	-6 (18)
C(2A)	-43742 (49)	54234 (44)	62215 (36)	817 (41)	636 (35)	310 (24)	502 (33)	-49 (24)	21 (23)
C(3A)	-36504 (48)	57959 (41)	66690 (37)	798 (40)	481 (29)	380 (26)	379 (29)	14 (25)	-40 (21)
C(4A)	-30785 (42)	54820 (42)	66808 (37)	529 (31)	529 (31)	376 (25)	154 (25)	-7 (21)	-100 (22)
C(5A)	-31841 (37)	48209 (39)	62035 (35)	437 (26)	506 (28)	384 (24)	218 (23)	-24 (19)	-84 (20)
C(6A)	-38922 (37)	44789 (32)	57209 (30)	531 (27)	340 (22)	260 (20)	200 (20)	45 (18)	45 (16)
N(7A)	-39707 (28)	38322 (27)	52367 (24)	437 (20)	415 (20)	265 (16)	229 (17)	-45 (14)	-55 (13)
N(8A)	-46438 (27)	34806 (27)	47834 (24)	406 (20)	390 (19)	291 (17)	178 (16)	-3 (14)	16 (14)
N(9A)	-44390 (28)	30193 (28)	43464 (25)	438 (20)	418 (20)	303 (17)	236 (17)	-30 (14)	-60 (4)
C(10A)	-50532 (33)	25112 (32)	38051 (30)	387 (23)	326 (21)	308 (20)	136 (18)	-33 (16)	-4 (16)
C(11A)	-47699 (41)	21592 (42)	32626 (36)	546 (31)	564 (31)	379 (25)	279 (26)	-72 (21)	-118 (22)
C(12A)	-53403 (51)	16841 (48)	27097 (42)	784 (42)	669 (38)	462 (30)	431 (34)	-124 (28)	-160 (26)
C(13A)	-61850 (46)	15413 (42)	26886 (39)	629 (35)	511 (31)	422 (27)	242 (28)	-158 (24)	-87 (23)
C(14A)	-64702 (40)	18810 (41)	32311 (40)	464 (29)	496 (29)	432 (27)	114 (24)	-80 (22)	-16 (23)
C(15A)	-59046 (35)	23606 (37)	38031 (34)	381 (24)	484 (27)	387 (23)	159 (21)	17 (18)	-22 (19)
C(1B)	23994 (43)	-17046 (44)	13405 (34)	678 (35)	699 (35)	332 (23)	499 (31)	-81 (22)	-98 (22)
C(2B)	25525 (51)	-10647 (47)	18633 (39)	854 (43)	703 (38)	392 (27)	558 (36)	42 (27)	-39 (25)
C(3B)	31714 (45)	-8699 (41)	24096 (34)	681 (35)	539 (30)	302 (23)	315 (27)	8 (22)	-85 (20)
C(4B)	36064 (36)	-13405 (35)	24506 (30)	494 (27)	422 (24)	264 (20)	196 (21)	17 (18)	-27 (17)
C(5B)	34605 (34)	-19664 (32)	19321 (29)	436 (24)	392 (23)	246 (19)	208 (20)	-18 (16)	-16 (16)
C(6B)	28637 (31)	-21479 (31)	13778 (27)	373 (21)	382 (21)	217 (17)	217 (18)	-1 (15)	22 (14)
N(7B)	27582 (27)	-27795 (28)	8628 (23)	427 (20)	450 (20)	236 (15)	256 (17)	-30 (13)	-33 (13)
N(8B)	20892 (27)	-30836 (28)	4122 (24)	383 (19)	434 (20)	293 (16)	211 (16)	-45 (14)	-46 (14)
N(9B)	22528 (27)	-35610 (28)	-282 (25)	389 (19)	431 (20)	292 (16)	196 (17)	-57 (14)	-62 (14)
C(10B)	16260 (33)	-40689 (32)	-5546 (29)	419 (23)	362 (22)	231 (18)	144 (19)	-39 (16)	3 (15)
C(11B)	18500 (40)	-44679 (38)	-10800 (36)	555 (30)	469 (27)	398 (25)	272 (25)	-111 (21)	-93 (20)
C(12B)	12442 (51)	-49686 (46)	-16060 (39)	840 (44)	649 (36)	354 (26)	403 (34)	-168 (26)	-160 (24)
C(13B)	4151 (47)	-50793 (47)	-15924 (42)	633 (37)	628 (36)	437 (29)	228 (30)	-260 (26)	-89 (25)
C(14B)	1961 (45)	-46601 (51)	-10802 (39)	568 (39)	772 (42)	398 (32)	294 (32)	-160 (24)	-76 (27)
C(15B)	7923 (38)	-41544 (38)	-54102 (34)	386 (28)	598 (28)	363 (22)	188 (24)	-99 (19)	-62 (19)
C(1C)	-3104 (65)	-23065 (45)	15567 (39)	1464 (69)	497 (32)	314 (26)	493 (40)	33 (32)	-68 (22)
C(2C)	-7261 (98)	-29163 (58)	10100 (52)	1832 (108)	600 (44)	408 (36)	476 (57)	-37 (50)	-184 (31)
C(3C)	-13463 (94)	-28661 (78)	6126 (66)	1335 (91)	950 (66)	550 (48)	240 (63)	-16 (52)	-327 (47)
C(4C)	-15542 (78)	-22184 (94)	6940 (61)	1086 (72)	1610 (100)	637 (48)	650 (73)	-246 (46)	-451 (58)
C(5C)	-11108 (54)	-15773 (63)	12609 (45)	788 (44)	1184 (61)	460 (32)	523 (45)	-211 (30)	-423 (37)
C(6C)	-5201 (40)	-16596 (38)	16838 (31)	593 (31)	465 (27)	241 (20)	181 (24)	37 (19)	-76 (18)
N(7C)	-1236 (29)	-10463 (29)	22463 (26)	499 (22)	456 (21)	297 (17)	268 (19)	-30 (15)	-30 (14)
N(8C)	4114 (30)	-11318 (29)	26752 (24)	496 (22)	466 (22)	293 (17)	278 (19)	7 (15)	8 (14)
N(9C)	6604 (26)	-4817 (26)	31348 (24)	356 (18)	375 (19)	331 (17)	118 (15)	-21 (13)	-48 (14)
C(10C)	13219 (32)	-3271 (35)	36384 (28)	370 (22)	523 (26)	224 (18)	224 (20)	21 (15)	22 (16)
C(11C)	15306 (36)	3268 (36)	41551 (31)	470 (26)	478 (25)	301 (20)	231 (22)	-15 (17)	12 (18)
C(12C)	21753 (41)	4990 (43)	46675 (36)	532 (30)	605 (33)	365 (25)	225 (26)	-84 (21)	-27 (22)
C(13C)	26363 (42)	531 (50)	46457 (38)	494 (30)	815 (40)	411 (26)	335 (29)	-44 (21)	57 (26)
C(14C)	24216 (47)	-6018 (55)	41336 (39)	698 (36)	987 (47)	419 (27)	641 (37)	37 (25)	74 (29)
C(15C)	17595 (45)	-7985 (46)	36301 (36)	700 (35)	791 (39)	312 (23)	529 (33)	-19 (22)	-25 (23)

Table 2 (*cont.*)(b) Hydrogen atoms. Values are $\times 10^4$. Atoms were assigned $B = 5\text{--}80$.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1A)	-0.5071	0.4465	0.5370
H(2A)	-0.4834	0.5680	0.6232
H(3A)	-0.3549	0.6320	0.7040
H(4A)	-0.2508	0.5774	0.7049
H(5A)	-0.2716	0.4574	0.6190
H(11A)	-0.4098	0.2270	0.3270
H(12A)	-0.5118	0.1405	0.2279
H(13A)	-0.6609	0.1161	0.2246
H(14A)	-0.7140	0.1764	0.3230
H(15A)	-0.6131	0.2638	0.4234
H(1B)	0.1925	-0.1837	0.0902
H(2B)	0.2212	-0.0681	0.1832
H(3B)	0.3288	-0.0373	0.2807
H(4B)	0.4087	-0.1190	0.2884
H(5B)	0.3812	-0.2328	0.1956
H(11B)	0.2523	-0.4385	-0.1084
H(12B)	0.1414	-0.5302	-0.2031
H(13B)	-0.0072	-0.5491	-0.2001
H(14B)	-0.0478	-0.4769	-0.1833
H(15B)	0.0614	-0.9384	-0.0128
H(11C)	0.1163	0.0687	0.4158
H(12C)	0.2347	0.1017	0.5066
H(13C)	0.3150	0.0189	0.5040
H(14C)	0.2792	-0.0958	0.4137
H(15C)	0.1584	-0.1314	0.3225

Table 3. Bond distances (\AA) and angles ($^\circ$) with their standard deviations

	<i>A</i>	<i>B</i>	<i>C</i>
Co—N(7)	1.925 (5)	1.904 (5)	1.926 (5)
Co—N(9)	1.913 (5)	1.920 (5)	1.927 (5)
C(1)—C(2)	1.388 (10)	1.405 (11)	1.390 (15)
C(1)—C(6)	1.384 (9)	1.382 (9)	1.389 (11)
C(2)—C(3)	1.379 (11)	1.397 (11)	1.354 (20)
C(3)—C(4)	1.366 (11)	1.379 (10)	1.365 (21)
C(4)—C(5)	1.397 (10)	1.385 (8)	1.450 (16)
C(5)—C(6)	1.400 (9)	1.386 (8)	1.364 (12)
C(6)—N(7)	1.399 (7)	1.404 (7)	1.408 (8)
N(7)—N(8)	1.325 (7)	1.318 (7)	1.295 (7)
N(8)—N(9)	1.317 (7)	1.301 (7)	1.312 (7)
N(9)—C(10)	1.416 (7)	1.406 (7)	1.407 (7)
C(10)—C(11)	1.396 (9)	1.368 (9)	1.397 (8)
C(10)—C(15)	1.382 (9)	1.386 (9)	1.383 (6)
C(11)—C(12)	1.384 (11)	1.369 (11)	1.391 (9)
C(12)—C(13)	1.376 (12)	1.369 (12)	1.380 (11)
C(13)—C(14)	1.385 (10)	1.369 (11)	1.390 (12)
C(14)—C(15)	1.409 (7)	1.398 (10)	1.393 (11)
N(7)—Co—N(9)	65.1 (2)	64.7 (2)	64.5 (2)
Co—N(7)—N(8)	95.6 (3)	96.4 (3)	96.0 (4)
Co—N(9)—N(8)	96.4 (3)	96.2 (3)	95.4 (3)
N(7)—N(8)—N(9)	102.9 (4)	102.7 (4)	104.1 (5)
C(6)—N(7)—N(8)	119.2 (5)	119.4 (5)	118.4 (5)
N(8)—N(9)—C(10)	117.9 (5)	119.3 (5)	118.9 (5)
C(5)—C(6)—C(1)	120.4 (6)	119.9 (5)	121.6 (7)
C(6)—C(1)—C(2)	119.4 (6)	119.0 (6)	119.5 (9)
C(1)—C(2)—C(3)	120.3 (7)	120.7 (7)	119.1 (10)
C(2)—C(3)—C(4)	120.5 (7)	119.3 (6)	123.5 (12)
C(3)—C(4)—C(5)	120.4 (7)	119.9 (6)	117.6 (12)
C(4)—C(5)—C(6)	118.8 (6)	121.1 (5)	118.4 (10)
C(15)—C(10)—C(11)	120.3 (6)	120.8 (6)	120.3 (5)
C(10)—C(11)—C(12)	119.4 (7)	120.0 (7)	119.9 (6)
C(11)—C(12)—C(13)	121.4 (7)	120.1 (7)	120.1 (6)
C(12)—C(13)—C(14)	119.3 (7)	120.1 (7)	119.7 (7)
C(13)—C(14)—C(15)	120.4 (7)	121.0 (7)	120.7 (8)
C(14)—C(15)—C(10)	119.2 (6)	117.9 (6)	119.3 (7)

trigonal elongation nor compression. On the other hand, the twist angle relating the triads of nitrogen atoms is 41.7° , as compared with 60° for octahedral symmetry and 0° for trigonal prismatic. By this criterion, the trigonal distortion is larger in Co(dpt)_3 than in tris(*trans*-1,2-diaminocyclopentane) cobalt (III) chloride tetrahydrate, for which Ito, Marumo & Saito (1971) reported a twist angle of 54.5° and an N—Co—N angle of 86.7° . This type of distortion is thus not unique to the dpt anion. Hilton & Wallwork (1968) have observed rather similar departures in $\text{Co(NO}_3)_3$. They report an O—Co—O bond angle of 68° and a reduction of the O—N—O angle nearest Co to 110° . Further, a review of nitrate structures by Addison, Logan, Wallwork & Garner (1971) points to a reduced O—N—O bond angle as a characteristic of several complexes containing symmetrically bidentate nitrate groups. Hence, it appears likely that the features of the Co(dpt)_3 structure cited as unusual by Corbett & Hoskins are,

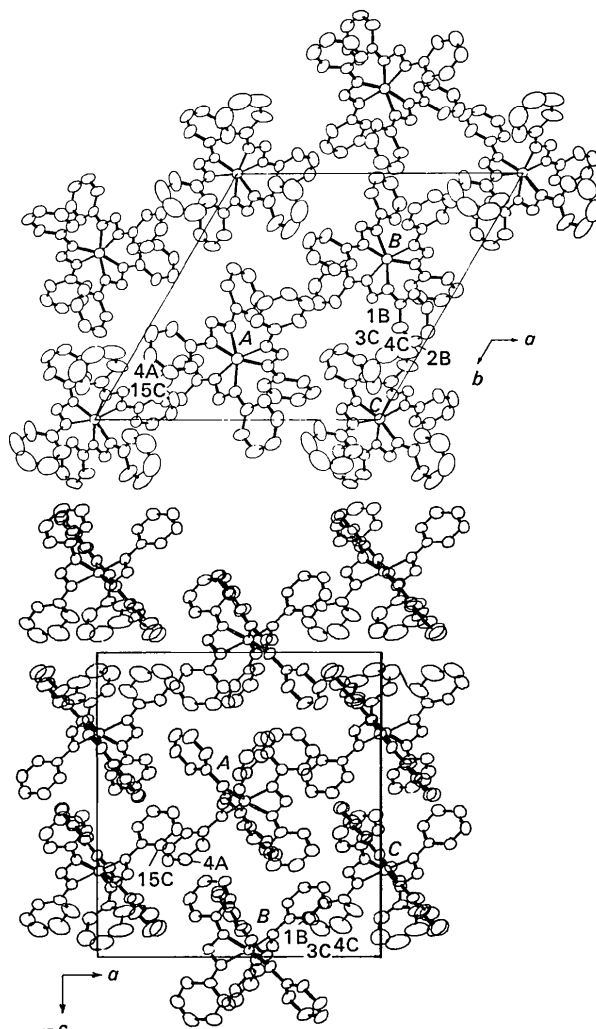


Fig. 2. Two views of the molecular packing in tris(diphenyltriazine)cobalt(III).

Table 4. *Relations between mean planes*

(a) Mean planes.

Equations of the mean planes are given in the form $ax' + by' + cz' + d = 0$, where x' , y' and z' are orthogonal coordinates (Å) derived from the fractional coordinates X , Y , Z by means of the transformation

$$\begin{pmatrix} 15.206 & 0 & 0 \\ -8.780 & 17.559 & 0 \\ 0 & 0 & 18.546 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

Plane	a	b	c	d	Max. dev. (Å)	
A	ε	0.5489	0.4801	-0.6842	-5.1133	0.029
	δ	0.4599	0.6539	-0.6007	-1.9239	0.010
	ζ	0.3146	0.7894	-0.5271	0.8335	0.012
B	ε	0.7244	0.3861	-0.5711	-0.7405	0.017
	δ	0.5097	0.6268	-0.5893	-3.3790	0.004
	ζ	0.3260	0.7454	-0.5814	-4.9790	-0.018
C	ε	0.7176	0.2681	-0.6428	-3.2103	-0.022
	δ	0.7731	0.2113	-0.5981	-2.9927	0.013
	ζ	0.6787	0.3945	-0.6194	-3.5060	-0.019

Table 4 (cont.)

(b) Intramolecular interplanar angles (°).

Planes	A	B	C
$\varepsilon\delta$	12.2	18.6	5.2
$\delta\zeta$	12.2	12.6	11.9
$\varepsilon\zeta$	24.2	31.1	7.7

(c) Intermolecular interplanar angles (°).

$\delta_A - \delta_B$	3.3
$\zeta_A - \zeta_B$	4.1
$\zeta_C - \varepsilon_B$	3.8
$\varepsilon_C - \varepsilon_B$	7.9
$\delta_C - \varepsilon_B$	10.5
$\zeta_C - \varepsilon_A$	9.7
$\delta_A - \zeta_B$	9.4

in fact, typical of octahedral complexes formed from bidentate ligands having short 'bite'.

The average Co-N bond length in trigonal $\text{Co}(\text{dpt})_3$ is 1.92 ± 0.01 Å, which may be compared with the value 1.94 Å reported by Corbett & Hoskins. The N-N bonds are equivalent in the present structure, with average length 1.31 ± 0.01 Å. This observation, coupled with the somewhat short C-N bond length (average 1.407 ± 0.004 Å), suggests delocalization of the π electrons. The parameters of the phenyl rings exhibit some variation, but no systematic deviations. The average bond distance and angle, 1.39 ± 0.01 Å and $120.0 \pm 0.8^\circ$, are quite reasonable, particularly in view of the fact that no attempt was made to correct the positional parameters for anisotropic thermal motion.

Since a molecule of each hand is located on each threefold axis, it might be anticipated that all $\text{Co}(\text{dpt})_3$ moieties would have approximately the same molecular conformation, and that the molecules would be uniformly spaced along z . This is not the case. Separations larger and smaller than $c/2$ alternate, with the difference being 0.75 Å along the interior threefold axes and 1.43 Å along that at the origin. Further, each unique dpt molecule has a different conformation, as shown by the intramolecular interplanar angles appearing in Table 4(b). Corbett & Hoskins state that the phenyl groups of each ligand in the monoclinic $\text{Co}(\text{dpt})_3$

structure are twisted by approximately 20° with respect to each other, and with respect to the triazenido moiety. None of the molecules in the trigonal modification follows this description closely; however, molecules A and B have the largest angles between the normals to the ring planes, while molecule C is more nearly planar, and more nearly resembles the conformation reported for neutral dpt and for the anion in complexes with other metals. Despite the fact that each unique dpt has a different conformation, some of the planes of different molecules are approximately coplanar, as indicated in Table 4(c).

Some difficulty in achieving an efficient packing of the molecules may be anticipated from the observation that the three unique dpt molecules have different conformations, and that the molecular spacing along z is irregular. The molecular packing is illustrated in two orthogonal views in Fig. 2, which shows thermal ellipsoids at the 50% probability level. These are quite elongated for the ring C(1C)-C(6C). A calculation involving the atoms listed in Table 2 disclosed only one close intermolecular contact, H(4A) of symmetry (x, y, z) with H(15C) of symmetry $(y, y-x, -z)$, having a separation of 2.3 Å. However, when the remaining hydrogen atoms were inserted in their expected positions, H(3C) of symmetry (x, y, z) and H(1B) of symmetry $(y, y-x, -z)$ gave a calculated separation, 2.2 Å, significantly smaller than twice the van der Waals radius of hydrogen (2.4 Å). This repulsion is probably relieved in some of the molecules by displacement of the ring C(1C)-C(6C), which is reflected in the anisotropic thermal parameters for these atoms. It should be mentioned that our observation of this peculiarity is not restricted to one crystal specimen. Our analysis was begun with a somewhat smaller data set collected using a different crystal, and refinement below $R=0.20$ revealed a similar disturbance of the same ring.

We note, finally, that interpretation of the single-crystal polarized spectra of $\text{Co}(\text{dpt})_3$ should be facilitated by use of the trigonal modification, since for it the molecular and threefold axes coincide.

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Etude de la Conformation d'Aldéhydes Thiophéniques et Furanniques: Structure Cristalline du Formyl-2 Bromo-4 Furanne

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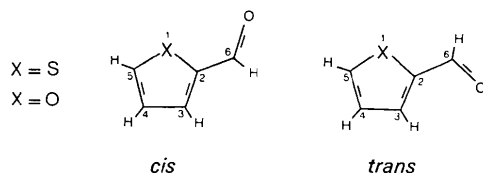
(Reçu le 25 septembre, accepté le 20 octobre 1972)

Crystal of 2-formyl-4-bromofuran are monoclinic with space group $P2_1/c$ and have eight molecules in the unit cell of dimensions $a = 9.48$, $b = 7.56$, $c = 16.10$ Å, $\beta = 92^\circ$. The structure has been determined by the heavy-atom method and refined by least-squares techniques on the base of three-dimensional photographic data with $R = 0.089$ for 1124 reflexions. The molecule is planar with the formyl group in the *cis* position. Two short distances $\text{Br} \cdots \text{O}$ of 3.06 Å show the existence of charge-transfer intermolecular contacts.

Introduction

L'étude en résonance magnétique nucléaire de la stéréospécificité des couplages entre protons séparés par cinq liaisons a fait l'objet de nombreuses études (Karabatsos & Vane, 1963; Sternhell, 1969). De tels couplages, dont l'existence est liée à une disposition *trans-trans* coplanaire des liaisons, ont été utilisés pour déterminer les conformations préférentielles d'aldéhydes aromatiques (Forsen & Akermark, 1963).

Les formyl-2 thiophène et formyl-2 furanne, aldéhydes hétérocycliques à caractère aromatique, qui, par suite de l'effet de conjugaison, possèdent deux conformations planes, *cis* ou *trans*, ont été particulièrement étudiés.



Dans une étude sur le furfural (formyl-2 furanne) en RMN à basse température, Dahlqvist & Forsen (1965)

ont attribué des constantes de couplage, entre le proton aldéhydique et les protons du cycles, en contradiction avec la règle du couplage stéréospécifique *trans-trans*. D'après ces auteurs, le furfural existerait, en solution, sous la forme d'un mélange des conformères *cis* et *trans* avec prépondérance de la conformation *trans*.

La connaissance exacte de la stéréospécificité des couplages dans les séries thiophéniques et furanniques était importante pour l'étude par RMN des aldéhydes substitués. Le problème a été repris par une étude simultanée en RMN à basse température (état liquide) et par la diffraction des rayons X (état solide) des formyl-2 bromo-4 thiophène et furanne. Il existe en effet une corrélation entre l'état d'équilibre conformationnel en phase liquide et la cristallisation du composé soumis à cet équilibre (Pethrick & Wyn-Jones, 1969): c'est en général le conformère le plus stable du point de vue thermodynamique qui cristallise (Mizushima, 1954; Sheppard, 1959).

Les formyl-2 bromo-4 thiophène et furanne ont été choisis parce qu'ils n'offrent en RMN qu'une seule possibilité de couplage: $J_{\text{CHO}-5}$ et parce que ces composés sont des solides cristallisés. *A priori*, l'introduction de l'atome de brome ne devrait pas avoir d'influence sur la libre rotation du groupement aldéhydique.

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