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The Crystal and Molecular Structure of Bis-(*N,N'*-π-cyclopentadienyl cobalt)-di-*tert*-butyl Urea, $(\pi\text{-}C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$

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The crystals of $(\pi\text{-}C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$ are orthorhombic, and the space group is *Fdd*2, with $a=9.10_1$, $b=17.97_3$, $c=23.61_6$ Å, and $Z=8$. The crystal structure was determined with use of Mo*Kα* counter data, the final *R* being 0.063 for 578 non-zero reflections. The molecules has a C_2 symmetry, and the carbonyl group lies exactly on the two-fold axis. Unexpectedly, the molecule has the local structure of *N,N'*-di-*t*-butyl urea, two nitrogen atoms being bridged to two cobalt atoms. The two crystallographically independent Co–N bonds are 1.942 and 1.951 Å, which are equal within the limits cf experimental error. Two cobalt atoms are directly bonded to each other at a distance of 2.371 Å, which is shorter than that of 2.47 Å found in $(CO)_6Co_2(C_2Ph_2)$.

Many polynuclear organometallic compounds which involve metal-metal bonds have been found, and some of them contain nitrogen or sulfur atoms bridging between the metal atoms. The bridge nitrogen or sulfur atoms in these complexes may stabilize the metal-metal bonds.

The $(\pi\text{-}C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$ complex was prepared according to the following reaction[1)] (Table 1).

Both complexes, III and IV, are presumed to take trigonal bipyramidal sturctures,[1)] having three cobalt atoms in the equatorial plane. Compound II was not identified as *N,N'*-di-*t*-butyl urea until the structure analysis of the complex I had been completed. According to such recent spectrochemical studies as IR, NMR, and mass spectra, the two structures shown in Fig. 1 have been proposed for the complex I.[1)]

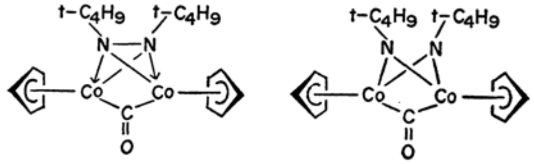

Fig. 1. Two proposed structures for the complex I.

To determine the exact structure of this compound involving the feature of coordination around the cobalt atom, the crystal structure analysis of the complex I, $(C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$, was undertaken by means of X-ray diffraction.[2)]

Experimental

The crystal is dark green and has a needle-like shape elongated along the *c* axis. The melting point is 165—168°C, and around this temperature the crystal sublimes appreciably.

The approximate cell dimensions were determined by taking Weissenberg photographs with nickel-filtered Cu*Kα* radiation. The space group was uniquely determined as *Fdd*2 from the following systematic absences

TABLE 1. REACTION BETWEEN $(t\text{-}C_4H_9N)_2S$ AND $\pi\text{-}C_5H_5Co(CO)_2$

				Yield
$(t\text{-}C_4H_9)_2S$		+ $(\pi\text{-}C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$	(I)	2.1%
+	⟶	+ $(t\text{-}C_4H_9NH)_2CO$	(II)	1.0
$\pi\text{-}C_5H_5Co(CO)_2$		$(\pi\text{-}C_5H_5Co)_2S_2$	(III)	22.9
		+ $(\pi\text{-}C_5H_5Co)_3S(CO)$	(IV)	4.7

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1) S. Otsuka, A. Nakamura and T. Yoshida, *Inorg. Chem.*, **7**, 261 (1968).

2) Y. Matsuura, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Otsuka, A. Nakamura and T. Yoshida, *Chem. Commun.*, **1967**, 1122.

of reflections:

$hkl;\ h + k \neq 2n,\ k + l \neq 2n;$

$0kl;\ k + l \neq 4n$ and

$h0l;\ l + h \neq 4n$

The precise determination of the unit cell dimensions and the collection of the intensity data were carried out by the use of a G. E. XRD-5 diffractometer equipped with a single crystal orienter.*4 Zirconium-filtered Mo$K\alpha$ radiation (λ=0.7107 Å) was used. The crystallographic data of this compound are listed in Table 2.

TABLE 2. CRYSTALLOGRAPHIC DATA OF $(\pi\text{-}C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$

Orthorhombic	$M = 418.1$
$a = 9.10_1$ Å	$Z = 8$
$b = 17.97_3$ Å	$D_m = 1.46\ \mathrm{g \cdot cm^{-3}}$
$c = 23.61_6$ Å	$D_x = 1.44\ \mathrm{g \cdot cm^{-3}}$
$V = 3862.9$ Å	Space Group *Fdd*2

Within the limits of $2\theta \leq 45°$, 641 independent reflections were obtained, but of these 83 were too weak to be measured.

The crystal used had dimensions of 0.10×0.12×0.10 mm. The linear absorption coefficient, μ, was 18.0 cm^{-1}. No correction for absorption was made because of the negligibly small variation in the transmission of X-rays over the observed angular range, while the corrections for Lorentz and polarization factors were made in the usual way.

Structure Determination

As may be seen in Table 2, the unit cell contains eight molecules. Since the general position in the *Fdd*2 space group is sixteen-fold, the whole molecule should possess a C_2 symmetry and the carbonyl group must lie on the two-fold axis.

The position of the cobalt atom was easily found from a three-dimensional Patterson function. A three-dimensional electron density distribution based on the phase of the cobalt atom revealed the positions of all the light atoms other than hydrogen. The positions of these atoms were also confirmed by the minimum function method.

The refinements of the positional and thermal parameters of the 13 non-hydrogen atoms were carried out by means of the least-squares procedure. The first three cycles with isotropic temperature factors for all atoms except hydrogen gave the discrepancy factor of R=0.11 for non-zero reflections. The next three cycles, of a similar refinement, with an anisotropic temperature factor for only the Co atom, gave R=0.083, while five more cycles with anistorpic temperature factors for all the atoms reduced the R to 0.063 (0.093 for all reflections). The quantity minimized was $\sum w(\Delta F)^2$. Throughout the refinement procedure, the following weighting scheme was applied:

$w = 1.0$ for $F_o \geqq 29$, and

$w = 0.2$ for $F_o < 29$ (marked by asterisks in Table 5).

The final atomic coordinates, together with their estimated standard deviations, are listed in Table 3. The thermal parmeters are shown in Table 4, while the observed and calculated structure factors are given in Table 5. Figure 2 shows a composite diagram of the three-dimensional electron density distribution viewed along the b axis.

TABLE 3. ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS, $\sigma(10^{-3}$ Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Co	0.0852	2	0.0499	2	0.0000	6
N	0.0896	12	−0.0386	11	0.0471	11
C(1)	0.2065	16	−0.0897	16	0.0660	12
C(2)	0.1334	20	−0.1515	17	0.1038	19
C(3)	0.2770	18	−0.1259	18	0.0109	23
C(4)	0.3181	19	−0.0461	21	0.1007	20
C(5)	0.2492	28	0.1301	22	−0.0046	28
C(6)	0.1207	24	0.1581	18	−0.0258	24
C(7)	0.0729	24	0.1140	23	−0.0750	24
C(8)	0.1793	24	0.0580	24	−0.0815	22
C(9)	0.2835	22	0.0720	25	−0.0364	29
C(10)	0.0000	0	0.0000	0	0.0849	24
O	0.0000	0	0.0000	0	0.1348	16

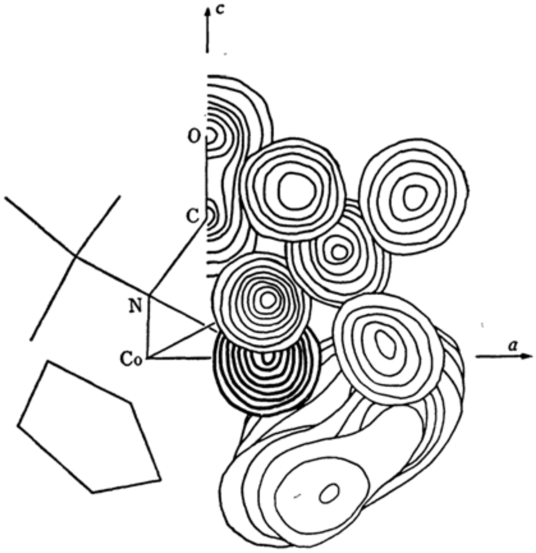

Fig. 2. A composite drawing of the final electron density of a molecule.

The Patterson function and the minimum function were calculated on a HITAC 5020E computer of the University of Tokyo, with programs written by one of the present authors (N. Y.). The least-squares refinement and other calculations were

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*4 The calculations for the goniostat setting were made on a NEAC 2101 computer with a program written by one of the present authors (T. U.).

TABLE 4. ANISOTROPIC THERMAL PARAMETERS
Parameters are expressed of the form: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\bar{B}$*
Co	0.0090	0.0025	0.0020	−0.0003	0.0009	0.0009	3.53
N	0.0092	0.0025	0.0009	0.0020	0.0005	0.0001	2.77
C(1)	0.0116	0.0029	0.0023	0.0045	−0.0016	0.0000	4.27
C(2)	0.0197	0.0030	0.0025	0.0017	0.0023	0.0016	5.36
C(3)	0.0146	0.0042	0.0033	0.0061	0.0036	−0.0007	5.88
C(4)	0.0150	0.0056	0.0028	0.0009	−0.0065	0.0003	6.16
C(5)	0.0376	0.0062	0.0031	−0.0159	0.0069	0.0026	9.13
C(6)	0.0277	0.0028	0.0047	−0.0025	0.0072	0.0051	7.74
C(7)	0.0251	0.0060	0.0034	−0.0060	0.0047	0.0032	7.91
C(8)	0.0250	0.0068	0.0029	−0.0071	0.0072	0.0009	7.82
C(9)	0.0162	0.0078	0.0061	−0.0006	0.0098	0.0053	9.64
C(10)	0.0112	0.0020	0.0021	0.0003	0.0000	0.0000	3.68
O	0.0238	0.0061	0.0012	0.0072	0.0000	0.0000	6.16

* "Equivalent isotropic temperature factor"; obtained by averaging $4\beta_{11}/a^{*2}$, $4\beta_{22}/b^{*2}$, and $4\beta_{33}/c^{*2}$.

carried out on a IBM 7090 computer through the 'UNICON' project and a NEAC 2200 computer of this University with programs written by Dr. Tamaichi Ashida. The atomic scattering factors used in the calculations were taken from those of Hanson and his co-workers.[3)]

Results and Discussions

The skeleton of the molecule is shown in Figs. 3 and 4, as viewed along the *b* and *c* axes respectively.

Instead of the previously proposed structure, the complex takes an unexpectedly unique structure. The ligand molecule forms a urea-like structure. The two nitrogen atoms bridge to the two cobalt atoms, and the cobalt atoms are also bonded to each other. These bridge nitrogen atoms are themselves bridged by the carbonyl. Such a urea-like local structure formed in this molecule may be closely related to the formation of N,N'-di-*t*-butyl urea during the preparation of this compound; this complex may be regarded as an intermediate in the formation of the above-mentioned urea in the reaction between $(t\text{-}C_4H_9N)_2S$ and $\pi\text{-}C_5H_5Co(CO)_2$ (Table 1). As has been stated before, the whole molecule has a C_2 symmetry, and the carbonyl lies exactly on the two-fold axis. As can be seen in Figs. 3 and 4, there are approximately two verticalmirror planes, perpendicular to each other in the molecule, and the molecule has a quasi-C_{2v} symmetry.

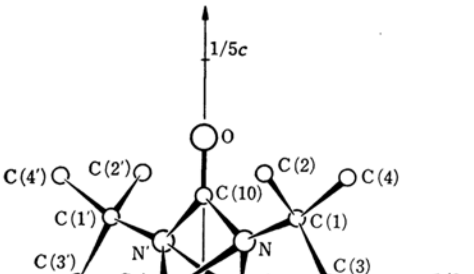

Fig. 3. The molecular structure of $(\pi\text{-}C_5H_5Co)_2\text{-}(N\text{-}t\text{-}C_4H_9)_2CO$.

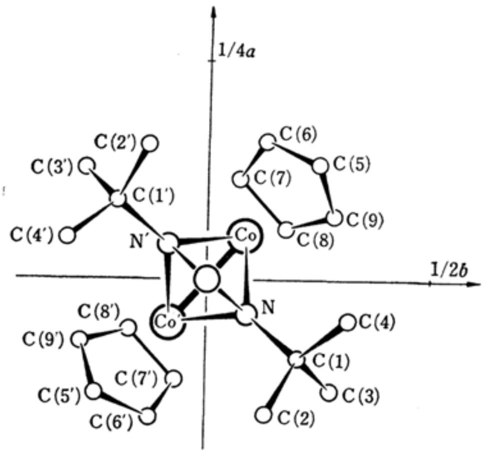

Fig. 4. The skeleton of the molecule; viewed down along the *c* axis.
The molecule has a quasi-C_{2v} symmetry.

The intramolecular bond lengths and angles are summarized in Table 6. In this table, the numbering of atoms is the same as in Figs. 3 and 4.

The Co–Co distance of 2.371 Å is shorter than

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3) H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

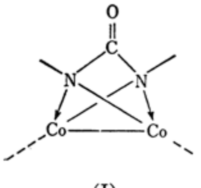
4) W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).

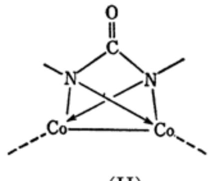
Table 5. The observed and calculated structure factors (×10)

L	FO	FC
H,K= 0 0		
4	402	416
8	326	310
12	272	274
16	184	178
20	130	127
24	90	79
H,K= 2 0		
2	46	35
6	94	101
10	45	48
14	79	80
18•	23	29
22	66	64
H,K= 4 0		
0	129	124
4	124	116
8	77	82
12	81	72
16	52	57
20	55	60
H,K= 6 0		
2	231	242
6	211	213
10	104	99
14	112	106
18	111	104
H,K= 8 0		
0	63	57
4	49	46
8	31	27
12	38	36
H,K= 1 1		
1	337	344
3	418	416
5	120	114
7	174	173
9	125	121
11	136	134
13	135	129
15	131	129
17	77	73
19	62	68
21	58	58
23	67	67
25	44	36
H,K= 3 1		
1	146	136
3	61	62
5	45	40
7	113	110
9•	28	35
11	40	41
13	68	70
15•	0	18
17	36	45
19•	24	25
21•	0	9
H,K= 5 1		
1	175	180
3	188	189
5	173	176
7	115	113
9	123	123
11	93	94
13	45	46
15	41	44
17	69	73
19	62	70
21	47	57
H,K= 7 1		
1	82	81
3	91	92
5	90	91
7	41	41
9	48	48
11	47	52
13	58	54
15	63	64
17	48	41
H,K= 0 2		
2	515	518
6	131	127
10	157	164
14	182	174
18	82	91
22	99	99
H,K= 2 2		
0	127	134
2	290	280
4	132	121
6	196	183
8	160	153
10	157	157
12	69	68
14	119	120
16	55	67
18•	23	30
20	49	52
22	37	33
24•	27	36
H,K= 4 2		
0	155	150
2	122	118
4	127	124
6	138	137
8	79	80
10	82	82
12	86	89
14	35	48
16	78	76
18	58	62
20	32	27
22	43	35
H,K= 6 2		
0	136	140
2•	25	19
4	182	189
6•	21	11
8	107	104
10	49	50
12	68	69
14•	0	12
16	90	87
18•	0	18
H,K= 8 2		
0	63	52
2	46	52
4	50	66
6	31	32
8	75	77
10	42	40
12	57	56
14•	0	18
H,K= 1 3		
1	258	277
3	137	119
5	337	324
7	106	99
9	145	136
11	94	101
13	82	90
15	88	90
17	61	62
19	37	37
21	50	52
23	46	50
H,K= 3 3		
1	131	130
3	246	227
5	176	168
7	38	49
9	206	199
11	129	135
13	132	131
15	115	105
17	70	75
19	30	38
21	41	43
H,K= 5 3		
1	97	95
3	119	116
5	63	63
7	116	114
9	56	62
11	51	53
13	49	59
15	29	31
17	54	59
19	65	60
21•	27	29
H,K= 7 3		
1	78	81
3	91	76
5	70	63
7	72	78
9	46	54
11	47	52
13	49	51
15•	0	15
17	44	50
H,K= 9 3		
1	32	37
3	66	64
5	61	46
7	58	58
9	48	44
H,K= 0 4		
0	108	93
4	113	104
8	56	64
12	39	39
16•	0	27
20	55	58
24•	0	35
H,K= 2 4		
0	280	267
2	236	226
4	97	120
6	140	131
8	254	253
10	44	55
12	253	244
14	57	67
16	105	98
18•	0	21
20	73	74
22•	0	28
24	39	40
H,K= 4 4		
0	39	35
2	181	198
4	148	143
6	208	227
8	48	54
10	143	148
12	48	44
14	149	139
16•	23	38
18	81	75
20•	0	31
22	34	37
H,K= 6 4		
0	37	26
2	45	38
4•	21	22
6	56	57
8•	22	10
10•	0	19
12•	0	9
14•	0	22
16•	0	22
18	38	34
H,K= 8 4		
0•	0	12
2	71	71
4	35	23
6	100	104
8	37	27
10	91	94
12•	27	6
H,K= 1 5		
1•	25	52
3	192	172
5	86	83
7	84	83
9	133	127
11	86	93
13	103	97
15	56	59
17•	22	32
19•	0	21
21	40	46
H,K= 3 5		
1	183	175
3	73	84
5	164	164
7	217	218
9	200	208
11	193	189
13	129	121
15	95	98
17	93	98
19	75	68
21	37	41
H,K= 5 5		
1	67	59
3	65	56
5	120	112
7	80	73
9	49	37
11	66	68
13•	28	27
15	58	54
17•	0	10
19•	0	18
H,K= 7 5		
1	47	41
3	60	62
5	41	45
7	49	51
9	56	63
11	48	54
13	59	54
15•	0	31
H,K= 9 5		
1	64	55
3	67	60
5	70	63
7	68	63
H,K= 0 6		
2	148	156
6	86	82
10•	25	34
14	70	73
18	53	50
22•	0	14
H,K= 2 6		
0	91	91
2	182	186
4	71	79
6	189	188
8	86	80
10	261	262
12	45	57
14	139	135
16•	0	21
18	87	84
20•	0	26
22	47	46
H,K= 4 6		
0	101	102
2•	23	6
4	212	226
6	39	39
8	200	204
10	54	54
12	120	118
14	40	54
16	95	95
18•	0	13
20	42	43
H,K= 6 6		
0	60	65
2•	27	20
4•	22	28
6	45	25
8	40	44
10•	24	23
12•	24	29
14•	0	20
16•	26	28
18•	0	11
H,K= 8 6		
0	57	57
2	36	39
4	73	81
6•	0	6
8	82	86
10•	0	22
12	84	71
H,K= 1 7		
1	118	117
3	177	160
5	134	136
7	158	159
9	66	71
11	112	113
13	87	89
15	59	72
17	85	85
19•	25	36
21•	0	28
H,K= 3 7		
1	82	85
3	114	123
5	152	157
7	225	220
9	131	125
11	117	121
13	94	93
15	83	82
17•	0	29
19	48	47
21	43	34
H,K= 5 7		
1	81	75
3	84	76
5	68	69
7	79	77
9	82	87
11	55	60
13	30	36
15	31	45
17•	26	33
19•	27	30
H,K= 7 7		
1	71	79
3	38	38
5	65	69
7	43	48
9	70	67
11	62	58
13	38	37
15	39	40
H,K= 9 7		
1	44	42
3	44	38
H,K= 0 8		
0	169	178
4	195	195
8	112	110
12	121	112
16	89	76
20	86	76
H,K= 2 8		
0	120	130
2	116	115
4	158	166
6	194	196
8	133	143
10	104	101
12	106	112
14	35	48
16	65	64
18	59	64
20•	0	18
H,K= 4 8		
0	136	145
2	57	52
4	105	100
6	126	130
8	112	114
10	84	80
12	86	87
14	51	56
16	40	44
18•	0	32
20•	0	32
H,K= 6 8		
0	36	37
2	112	113
4	33	36
6	95	100
8•	24	18
10	63	61
12•	0	5
14	53	58
16•	0	14
H,K= 8 8		
0	46	55
2	49	50
4•	26	28
6	60	50
8	39	37
10	52	48
H,K= 1 9		
1	153	159
3	165	167
5	180	181
7	126	135
9	134	132
11	60	63
13	88	94
15	72	76
17	46	54
19	63	65
21	51	52
H,K= 3 9		
1	68	68
3	65	54
5	67	68
7	61	59
9	75	77
11•	27	32
13•	0	22
15	38	32
17•	0	20
19•	0	9
21•	0	10
H,K= 5 9		
1	123	130
3	92	92
5	68	68
7	82	88
9	71	78
11	46	50
13	36	45
15•	26	48
17•	0	27
H,K= 7 9		
1	71	65
3	82	78
5	54	55
7	74	76
9	42	45
11	47	47
13	48	49
H,K= 0 10		
2	277	289
6	201	203
10	187	187
14	66	64
18	118	115
H,K= 2 10		
0	57	57
2•	0	8
4	140	142
6	29	33
8	56	52
10•	0	15
12	46	51
14•	0	16
16	56	56
18•	0	5
20•	0	36
H,K= 4 10		
0	34	30
2	133	132
4	46	46
6	65	63
8•	0	2
10	73	71
12•	0	17
14	44	36
16•	0	11
18	47	28
H,K= 6 10		
0	140	145
2	30	30
4	135	137
6•	0	3
8	94	97
10•	0	5
12	57	71
14•	0	12
H,K= 8 10		
0•	0	9
2	33	30
4•	0	10
6•	28	26
H,K= 1 11		
1	131	136
3	134	135
5	139	139
7	111	105
9	69	69
11	62	60
13	47	53
15	61	62
17	44	52
19	77	66
H,K= 3 11		
1	42	36
3	55	56
5	41	39
7	44	52
9•	28	32
11•	0	20
13•	0	11
15•	0	16
17•	0	20
19•	0	17
H,K= 5 11		
1	126	125
3	94	91
5	68	68
7	55	62
9	56	53
11	36	34
13	65	61
15•	27	34
H,K= 7 11		
1	53	56
3	49	51
5	57	55
7	33	41
9	48	43
H,K= 0 12		
0	153	164
4	171	177
8	130	133
12	108	97
16	90	88
H,K= 2 12		
0	97	98
2	63	62
4	106	109
6	49	44
8	51	56
10•	28	19
12	57	55
14	35	37
16	41	43
18	33	36
H,K= 4 12		
0	73	71
2	63	60
4	44	44
6	77	78
8•	24	18
10	43	44
12•	25	23
14•	26	30
16•	0	33
H,K= 6 12		
0•	0	2
2	124	109
4•	0	15
6	93	83
8•	0	7
10	67	58
12•	0	11
H,K= 1 13		
1	73	82
3	78	80
5	67	74
7	54	60
9•	0	21
11	42	41
13	56	60
15•	26	33
17	58	62
H,K= 3 13		
1	73	71
3	75	74
5	72	77
7	88	85
9	58	61
11	65	57
13	52	55
15	47	45
17•	0	25
H,K= 5 13		
1	83	78
3	54	52
5	54	59
7	36	29
9	53	47
11	33	38
13•	28	35
H,K= 7 13		
1	44	42
3	44	35
5	49	22
H,K= 0 14		
2	48	51
6	47	54
10•	0	20
14	49	44
H,K= 2 14		
0	32	28
2	110	116
4	50	44
6	82	73
8•	0	12
10	109	102
12•	0	10
14	89	75
16•	0	22
H,K= 4 14		
0	66	58
2	50	44
4	102	94
6	36	23
8	96	85
10•	0	8
12	64	65
14•	28	27
H,K= 6 14		
0	47	45
2•	0	13
4•	0	20
6•	0	5
8•	0	13
H,K= 1 15		
1	56	44
3	42	44
5	42	33
7•	0	20
9•	0	28
11	55	54
13•	0	21
15	55	55
H,K= 3 15		
1	84	85
3	61	57
5	80	79
7	85	81
9	78	75
11	89	82
13	62	53
H,K= 5 15		
1•	0	27
3	46	38
5	43	33
7•	0	14
9	34	25
H,K= 0 16		
0•	24	19
4	35	37
8	48	52
12	47	55
H,K= 2 16		
0	104	99
2	31	21
4	79	78
6•	0	7
8	93	91
10•	0	11
12	80	78
H,K= 4 16		
0	32	28
2	63	66
4•	0	8
6	88	74
8•	19	18
H,K= 1 17		
1	41	43
3•	0	38
5	45	49
7	37	42
9	43	47
11	39	35
H,K= 3 17		
1	46	39
3	74	66
5	57	54
7	39	43
9	63	59
H,K= 0 18		
2	63	71
6	61	62
H,K= 2 18		
0	43	51
2	43	41
4	39	31
6	59	56
H,K= 1 19		
1	56	49
3	52	58

that of 2.47 Å found in $(CO)_6Co_2(C_2Ph_2)$.[4] Such a shortening suggests that the metal-metal bond in this complex may be stabilized by the bridge nitrogens.

All the Co–N bonds, in which two pairs of crystallographically equivalent bonds are included, have the same distances within the limits of experimental error. These four Co–N bonds are in an essentially equal bonding state as a result of the resonance between two canonical structure I and II. The Co–N distances are similar to or somewhat shorter than those found in a number of cobalt-ammine complexes.[5]


(I)


(II)

The local features of the urea-like part of this compound are listed in Table 7 and compared with those of the urea.

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[5] Z. Dori, R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 483 (1967); M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 955 (1967); S. Baggio and L. N. Becka, *Chem. Commun.*, **1967**, 506.

TABLE 6. BOND DISTANCES AND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATIONS, (σ)

Atoms	Distance (Å)	σ (Å)	Atoms	Angle (deg.)	σ (deg.)
Co-Co'	2.371	0.012	N-Co-Co'	52.7	0.4
Co-N	1.942	0.013	N-Co-N'	66.8	0.5
Co-N'	1.951	0.013	N'-Co-Co'	52.3	0.4
N-C(1)	1.474	0.022	Co-N-Co'	75.1	0.5
C(1)-C(2)	1.574	0.027	Co-N-C(1)	134.3	1.0
C(1)-C(3)	1.590	0.029	Co'-N-C(1)	134.2	1.0
C(1)-C(4)	1.521	0.027	Co-N-C(10)	86.9	1.1
N-C(10)	1.394	0.026	Co'-N-C(10)	86.5	1.1
C(10)-O	1.180	0.028	C(1)-N-C(10)	122.5	1.5
Co-C(5)	2.078	0.029	N-C(1)-C(2)	107.8	1.4
Co-C(6)	2.064	0.025	N-C(1)-C(3)	107.3	1.5
Co-C(7)	2.115	0.025	N-C(1)-C(4)	109.0	1.4
Co-C(8)	2.112	0.025	C(2)-C(1)-C(3)	110.2	1.5
Co-C(9)	2.039	0.030	C(3)-C(1)-C(4)	112.5	1.6
C(5)-C(6)	1.369	0.037	C(4)-C(1)-C(2)	109.9	1.5
C(6)-C(7)	1.472	0.034	N-C(10)-N'	100.4	1.6
C(7)-C(8)	1.406	0.034	N-C(10)-O	129.8	2.1
C(8)-C(9)	1.449	0.038	C(5)-C(6)-C(7)	110.0	2.2
C(9)-C(5)	1.323	0.041	C(6)-C(7)-C(8)	105.6	2.1
			C(7)-C(8)-C(9)	104.2	2.2
			C(8)-C(9)-C(5)	113.6	2.6
N···N'	2.142	0.023	C(9)-C(5)-C(6)	106.5	2.5

It seems that the considerably shorter C–O distance, the longer C–N distance, and the smaller NCN angle of this molecule can be interpreted as being mainly due to the strong interaction among the nitrogen and cobalt atoms bound together.

TABLE 7. THE LOCAL FEATURES OF THE UREA-LIKE PART IN COMPARISON WITH UREA

	This compound	$(NH_2)_2CO$[6]
C-O	1.18_0	1.26_4 Å
C-N	1.47_4	1.33_6
∠NCN	$100._4$	118.0 deg.

The five carbon atoms of the cyclopentadienyl ring lie almost exactly on a plane; the maximum deviation from the plane being 0.003 Å. The equation of the least-squares plane in terms of rectangular coordinates is:

$$-0.52227X - 0.59808Y + 0.60790Z - 2.64618 = 0,$$

where $X=ax$, $Y=by$, and $Z=cz$.

The carbon atoms in the ring show a marked anisotropy in temperature factors, and these atoms have relatively large "equivalent isotropic temperature factors," as shown in the last column of Table 4. The electron-density distribution of the five carbon atoms of the cyclopentadienyl ring given in Fig. 2 shows a smearing of the electron density along the cyclopentadienyl ring which is similar to that in the ferrocene molecule. From these facts, it may be concluded either that the cyclopentadienyl ring is moving somewhat as a hindered rotator or that there exists an orientational disorder of the rings in the crystal. The

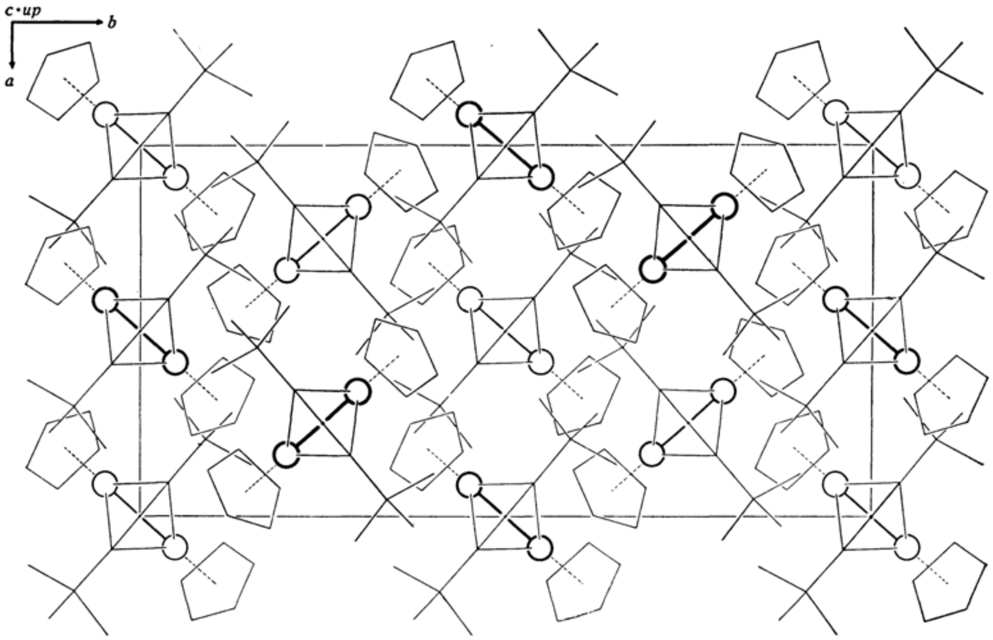

Fig. 5. The crystal structure of $(\pi\text{-}C_5H_5Co)_2(N\text{-}t\text{-}C_4H_9)_2CO$; viewed down along the c axis.

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[6] N. Sklar, M. E. Senko and B. Post, *Acta Cryst.*, **14**, 716 (1961).

Table 8. Some close intermolecular atomic contacts in the crystal
(those less than 4.0 Å are listed)

Contact	Distance
O-C(3^{i})	3.73 Å
C(4)-C(6^{ii})	3.86 Å
C(4)-C(7^{ii})	3.72 Å
O-C(7^{ii})	3.94 Å
C(2)-C(3^{iii})	3.87 Å
C(2)-C(8^{iii})	3.70 Å
O-C(3^{iii})	3.73 Å

Code for superscript:

i	$0.25-x$,	$0.25+y$,	$0.25+z$;
ii	$0.25+x$,	$0.25-y$,	$0.25+z$;
iii	$-0.25+x$,	$-0.25-y$,	$0.25+z$

plane of each cyclopentadienyl ring is at a distance of 1.704 Å from the cobalt atom.

Figure 5 shows the crystal structure viewed down the c axis. There are seven rather short intermolecular atomic contacts of less than 4.0 Å, the shortest one is 3.70 Å between C(2) and C(8^{iii}) (Table 8). All the other intermolecular distances are far longer than the sum of the van der Waals radii. The sublimation of this crystal around the melting point may be explained by this loose packing of the molecules.

The authors are very grateful to Professor Sei Otsuka and his co-workers of this University who gave them precious specimens.