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BONDING AND STRUCTURE IN CYCLOPENTADIENYLCOBALTMETALLACYCLE COMPLEXES. THE CRYSTAL STRUCTURES OF $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)_2C_6H_4]$ AND $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)SC_6H_4]$

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Summary

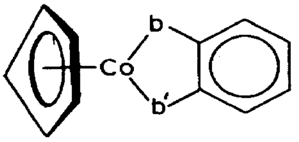
$[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)_2C_6H_4]$ (VII) crystallizes in the monoclinic space group $P2_1/c$ with a 9.530(3), b 15.960(4), c 9.987(3) Å, β 96.89(2)°, and $Z = 4$. Least-squares refinement of 2919 independent observed reflections, $F_{obs} \geqslant 3.0\sigma(F_{obs})$, gives R_F 5.20 and R_{wF} 5.57%.

$[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)SC_6H_4]$ (VIII) crystallizes in $P2_1/c$ with a 10.261(3), b 14.350(4), c 11.376(4) Å, β 113.65(2)°, and $Z = 4$. Least-squares refinement of 2546 independent observed reflections, $F_{obs} \geqslant 2.5\sigma(F_{obs})$, gives R_F 4.66 and R_{wF} 4.37%. Despite the low molecular symmetry, the cyclopentadienyl ring shows little tendency to distort to the "allyl-ene" or "diene" electron distribution. The metallacycle shows a slight preference for the imine electron distribution over other possibilities. Comparisons are made with other complexes having this molecular structure.

Introduction

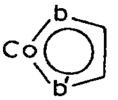
In recent years many organometallic reactions have been shown to proceed through metallacyclic intermediates or produce metallacyclic products. Important to understanding of the factors affecting the creation and stabilization of such structures is an understanding of the extent to which such cyclic species can support delocalized electron distributions.

The ground state electronic structure of Co in $(\eta^5\text{-}C_5R_5)Co(bb'C_6H_4)$ complexes (I) where R = H or CH_3, has been examined by ^{59}Co NQR spectroscopy [1,2].



(I)
(b, b' = O, S, Se, NR';
R' = H, CH_3, C_6H_5)

These studies suggest that σ-bonding dominates the primary bonding interaction between Co and (bb'C_6H_4). Several crystal structures are consistent with delocalized electron density in the five-membered metallacycle ring (i.e., II) with some contribution from III [3,4], while others suggest more localized bonding (i.e., III and/or IV) [5–8].



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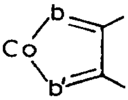

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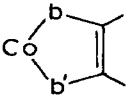
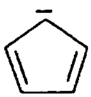


(IV)

A second interesting point is the fact that metallacyclopentadienyl complexes containing unequal C–C bond lengths in the η^5-C_5H_5 ring are known [9–11]. Allyl-ene and diene distortions are depicted in V and VI.

(V)



(VI)

Unbalanced population of the e_1'' HOMO set of the ring stemming from bonding to a metal fragment with less than C_3 symmetry or Jahn–Teller effects are thought to be responsible for these distortions.

In this paper two complexes of type I, [η^5-$C_5(CH_3)_5$]Co[$(NH)_2C_6H_4$] (VII) and [η^5-$C_5(CH_3)_5$]Co[$(NH)SC_6H_4$] (VIII) have been characterized structurally by X-ray crystallography. The results are discussed in terms of bonding modes in the metallacycle ring (II–IV) and distortions in the η^5-C_5H_5 ring, and are compared to other complexes of similar architecture. In addition, the extent to which ring permethylation affects these factors is discussed.

Experimental

The synthesis of VII and VIII is described elsewhere [1,2]. Regular-shaped single crystals were obtained by slow sublimation at 1 mmHg and were mounted on glass fibers with epoxy cement. Refined final unit cell parameters for VII and VIII were determined from the angular settings of 25 well-centered reflections ($20° \leq 2\theta \leq 30°$). Data collection details and unit cell parameters are given in Table 1.

The monoclinic space group, $P2_1/c$, was uniquely indicated for VII and VIII by systematic absences in the reflection data. Data collection, solution, and refinement employed routines in the P3 and SHELXTL (version 4.1) program packages (Nicolet Corp). Corrections for Lorentz and polarization effects were applied to the intensity data in each case. An empirical ψ-scan absorption correction was used for VII, but was deemed unnecessary for VIII based upon a more regular crystal shape and transmission data. Redundant data were averaged in each case to yield $R(I)$ 1.14 and 2.17% for VII and VIII, respectively.

[η^5-$C_5(CH_3)_5$]Co[$(NH)_2C_6H_4$] (VII)

The cobalt atom was located from a sharpened Patterson map. Least-squares

TABLE 1

CRYSTAL AND REFINEMENT DATA

Complex	VII	VIII
Formula	$C_{16}H_{21}CoN_2$	$C_{16}H_{20}CoNS$
Formula weight	300.28	317.34
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	9.530(3)	10.261(3)
b, Å	15.960(4)	14.350(4)
c, Å	9.987(3)	11.376(4)
β, deg.	96.89(2)	113.65(2)
V, Å^3	1508(1)	1534(1)
Z	4	4
ρ(calcd), g cm^{-3}	1.32	1.37
Temp., °C	25	25
Crystal dimensions (mm)	0.20 × 0.40 × 0.40	0.15 × 0.15 × 0.21
Abs. coeff., cm^{-1}	11.7	12.8
Diffractometer	Nicolet R3	
Radiation	Mo-K_α	
Variable scan speed, deg/min	3–20	5–20
Scan range, deg.	4–52	4–48
Scan technique	$\theta/2\theta$	ω
Data collected	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$
Weighting factor (g)[a]	0.00135	0.00033
Unique data/total data	2919/3263	2546/2661
Unique data, $F_0 \geqslant n\sigma(F_0)$	2130 (n = 3.0)	1944 (n = 2.5)
Standard reflections/ collected reflections-	3/150 (< 1% decay)	3/200 (< 1% decay)
R_F, R_{wF}, GOF	5.20, 5.57, 1.349	4.66, 4.37, 1.206

[a] Weight = $[\sigma^2(F)+g(F^2)]^{-1}$.

refinement of the metal atom position followed by difference Fourier syntheses located the remaining non-hydrogen atoms. Orientational disorder was observed in the $CpMe_5$ rings; they initially were refined as fixed pentagons with sides of 1.42 Å, but were unconstrained in the final cycles of least-squares refinement. The disorder was successfully resolved as two $CpMe_5$ rings staggered 36° about the Co–CNT axis. Refinement of the occupancies of the ring orientations indicated a two-fold preference for the orientation shown in Fig. 2. The phenyl and amine hydrogen atoms were located and refined isotropically. The hydrogen atoms on the $CpMe_5$ ring could not be unambiguously located from the torus of electron density surrounding the outer perimeter of the $CpMe_5$ ring; no attempt was made to incorporate these hydrogen atoms as idealized contributions. The largest peak in the final difference map was 0.3 e Å^{-3} located 0.53 Å from C(14).

[η^5-$C_5(CH_3)_5$]Co[(NH)SC_6H_4] (VIII)

The cobalt and sulfur atoms were located using the direct methods routine SOLV. Least-squares refinement of the metal and sulfur atom positions yielded all of the remaining nonhydrogen-atom positions. Following anisotropic refinement of these atoms, the hydrogen atoms were located and refined isotropically. The largest peak in the difference map was 0.3 e Å^{-3} located 0.54 Å from H(16a).

Description of structures

The atom coordinates, anisotropic thermal parameters, bond distances, and bond angles for VII and VIII are given in Tables 2–9.

[η^5-$C_5(CH_3)_5$]Co[$(NH)_2C_6H_4$] (VII)

The unit cell consists of four molecules packed in a head-to-tail arrangement as shown in Fig. 1. The molecular structure and atom labeling for VII with the $CpMe_5$ ring containing the carbon atoms in higher occupancy (0.667) is shown in Figure 2.

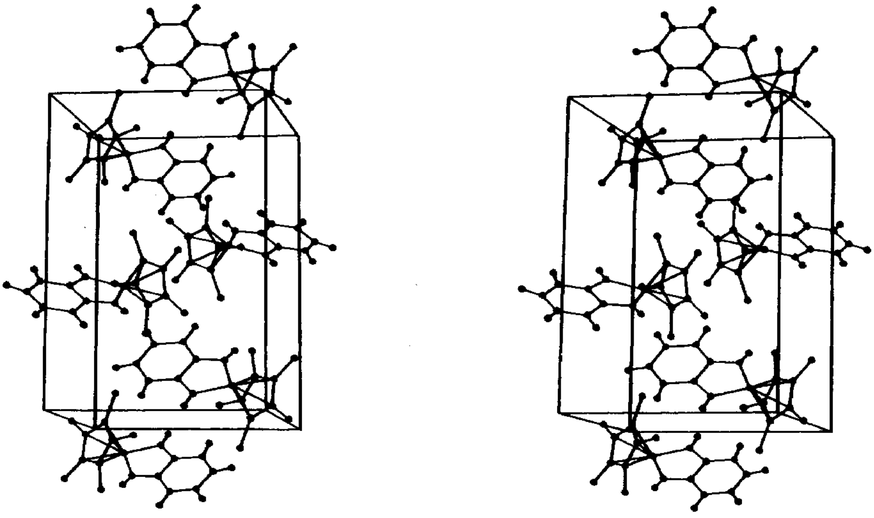


Fig. 1. A stereoview of the unit-cell packing of VII viewed along the *a*-axis.

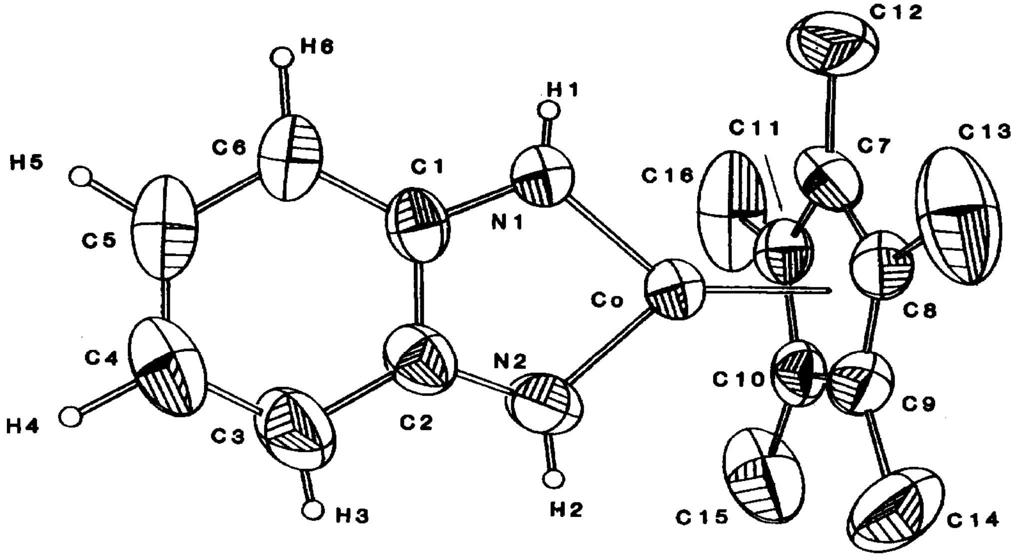


Fig. 2. The molecular structure and atom labelling for [η^5-$C_5(CH_3)_5$]Co[$(NH)_2C_6H_4$] (VII) showing 40% probability thermal ellipsoids.

The alternate orientation is rotated 36° and is coplanar with the major orientation. Although not crystallographically imposed, a pseudo-mirror plane containing the metallacycle and phenylene ring bisects the C(8)–C(9) or C(18)–C(17) bond vectors and contains C(7) or C(20), respectively, of the CpMe$_5$ rings in the two orientations.

Various distortions and inequalities in the CpMe$_5$ ring bond distances and angles (Table 5) for nominally equivalent parameters, e.g., a range of C–CH$_3$ distances spanning 0.1 Å and C–C–CH$_3$ bond angles (105.6(10)–109.5(8) for the higher occupancy ring and 99.3(18)–115.5(21) for the lower occupancy ring) are, to an uncertain degree, affected by the rotational disorder. In both (η^5-C$_5$H$_5$)-

TABLE 2

ATOM COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS (Å$^2 \times 10^3$) FOR [η^5-C$_5$(CH$_3$)$_5$]Co[(NH)$_2$C$_6$H$_4$] (VII) [a]

Atom	x/a	y/b	z/c	U_{iso} [a]
Co	2471(1)	924(1)	1973(1)	[b]
N(1)	931(4)	1598(2)	2029(3)	[b]
N(2)	2091(5)	646(3)	3672(4)	[b]
C(1)	309(4)	1584(3)	3185(4)	[b]
C(2)	994(5)	1033(3)	4129(4)	[b]
C(3)	477(7)	943(4)	5369(5)	[b]
C(4)	−657(7)	1382(4)	5665(5)	[b]
C(5)	−1342(5)	1931(3)	4729(5)	[b]
C(6)	−875(5)	2032(3)	3500(5)	[b]
C(7)	3087(15)	1177(8)	122(15)	[b]
C(8)	2798(8)	327(5)	196(7)	[b]
C(9)	3700(9)	−23(5)	1337(9)	[b]
C(10)	4573(9)	614(6)	1894(9)	[b]
C(11)	4251(4)	1337(8)	1215(13)	[b]
C(12)	2419(11)	1781(7)	−901(9)	[b]
C(13)	1675(11)	−158(8)	−745(11)	[b]
C(14)	3759(14)	−954(5)	1839(14)	[b]
C(15)	5662(10)	518(11)	3130(10)	[b]
C(16)	4912(14)	2208(8)	1452(15)	[b]
C(17)	3619(27)	1523(14)	698(24)	[b]
C(18)	2795(27)	837(11)	33(23)	[b]
C(19)	3035(14)	63(7)	708(13)	[b]
C(20)	4165(12)	256(7)	1759(11)	[b]
C(21)	4511(30)	1061(13)	1640(28)	[b]
C(22)	3664(31)	2425(10)	292(31)	[b]
C(23)	1588(21)	1025(16)	−1181(16)	[b]
C(24)	2290(23)	−748(11)	311(23)	[b]
C(25)	4810(22)	−394(12)	2770(19)	[b]
C(26)	5635(20)	1537(16)	2676(23)	[b]
H(1)	653(43)	1874(24)	1526(4)	58(11)
H(2)	2537(43)	300(25)	4153(39)	68(12)
H(3)	953(51)	522(32)	5782(47)	108(15)
H(4)	−1143(51)	1224(31)	6471(48)	113(16)
H(5)	−2118(56)	2234(3)	4859(54)	104(16)
H(6)	−1392(51)	2464(30)	2873(49)	926(15)

[a] Occupancy for C(7)–C(16) is 0.667 and C(17)–C(26) is 0.333. Correspondence by pseudo mirror plane: C(7)=C(20), C(8)=C(19), C(9)=C(18), C(10)=C(17), C(11)=C(21), C(12)–C(25), C(13)=C(24), C(14)=C(23), C(15)=C(22), C(16)=C(21). [b] Refined anisotropically, see Table 3.

Co[$(NH)_2C_6H_4$] [12] and [η^5-$C_5(CH_3)_5$]Co($O_2C_6H_4$) [8], insignificant differences exist in chemically related bond distances and angles. [η^5-$C_5(CH_3)_5$]-Co[$(NH)_2C_6H_3Cl$] also shows no significant distortion [13]. The CH_3 protons of VII exhibit a sharp singlet in the ^1H NMR spectrum of a $CDCl_3$ solution even at −77°C. We doubt, therefore, that VII contains a strongly distorted cyclopentadienyl ring.

The metallacycle ring is planar (maximum deviation 0.0068 Å) and is coplanar with the phenylene ring (interplanar angle 0.1°). The maximum deviation from planarity of the carbon atoms in the phenylene ring is 0.0037 Å. The Co–N and C–N bonds of VII are comparable in length to those in (η^5-C_5H_5)Co[$(NH)_2C_6H_4$] (1.830(10) ⟨av⟩, 1.344(15) Å ⟨av⟩, respectively) [12] and (η^5-C_5H_5)Co[(NH)-(NC_6F_5)C_6F_4] (1.844(3) ⟨av⟩, 1.356(9) Å ⟨av⟩, respectively) [3,4]. π-Electron delocalization in the metallacycle of the latter complex was suggested in part by comparing it to the Co–N "single bond" distance of 1.95–2.15 Å and a C–N "single bond" distance of 1.46–1.50 Å [3,4]. The Co–N–C bond angles (116–118°) are

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^3$) [a] FOR [η^5-$C_5(CH_3)_5$]Co[$(NH)_2C_6H_4$] (VII)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	54(1)	58(1)	52(1)	−1(1)	13(1)	−1(1)
N(1)	55(2)	75(2)	57(2)	10(2)	15(2)	7(2)
N(2)	94(3)	80(2)	63(2)	19(2)	22(2)	26(2)
C(1)	54(2)	63(2)	56(2)	−8(2)	14(2)	−15(2)
C(2)	83(3)	65(3)	56(2)	−4(2)	19(2)	1(2)
C(3)	132(5)	104(4)	67(3)	3(3)	43(3)	22(4)
C(4)	125(5)	95(4)	79(3)	−14(3)	50(3)	−16(4)
C(5)	74(3)	99(4)	106(4)	−27(3)	45(3)	−12(3)
C(6)	60(3)	96(4)	87(3)	−8(3)	29(2)	2(3)
C(7) [b]	98(9)	38(9)	74(7)	4(7)	48(6)	15(7)
C(8)	61(4)	58(5)	60(4)	−13(4)	20(3)	2(4)
C(9)	61(5)	64(5)	85(6)	6(4)	35(4)	12(4)
C(10)	55(5)	81(6)	64(5)	4(5)	11(4)	7(6)
C(11)	61(8)	36(10)	103(11)	10(6)	33(7)	9(7)
C(12)	137(9)	158(9)	88(6)	54(6)	43(6)	69(7)
C(13)	106(7)	216(12)	123(7)	−102(8)	47(6)	−71(8)
C(14)	189(12)	68(6)	218(13)	42(7)	127(11)	40(7)
C(15)	73(6)	260(14)	107(7)	19(9)	−13(5)	31(8)
C(16)	140(11)	100(8)	173(12)	−53(8)	88(9)	−53(8)
C(17) [c]	93(19)	26(10)	95(17)	16(10)	66(13)	30(11)
C(18)	84(14)	28(14)	46(8)	7(11)	4(8)	35(11)
C(19)	42(7)	36(6)	54(7)	3(5)	12(5)	5(5)
C(20)	49(7)	62(6)	56(6)	−9(5)	−4(5)	−2(5)
C(21)	76(12)	21(11)	104(16)	19(8)	10(11)	12(8)
C(22)	198(23)	57(9)	234(24)	39(13)	165(20)	19(12)
C(23)	95(12)	254(26)	44(8)	8(11)	4(8)	63(15)
C(24)	152(17)	102(12)	183(18)	−94(12)	109(15)	−72(12)
C(25)	137(15)	115(13)	120(14)	38(11)	30(11)	90(12)
C(26)	67(11)	191(21)	149(17)	−92(17)	16(11)	−49(13)

[a] The anisotropic temperature factor takes the form, $-2\pi^2(h^2a^{*2}U_{11}^2 + k^2b^{*2}U_{22}^2 + \ldots + 2hka^*b^*U_{12}^2 + \ldots)$. [b] Occupancy C(7)–C(16), 0.667. [c] Occupancy C(17)–C(26), 0.333.

approximately trigonal in all cases. As will be discussed shortly, the C–C bond lengths in the phenylene fragment evidence a long-short pattern consistent with the diimine ligand, III, although II is not ruled out [12].

TABLE 4

SELECTED BOND DISTANCES FOR $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)_2C_6H_4]$ (VII)

Co–N(1)	1.827(4)	Co–C(7)	2.045(15)
Co–N(2)	1.832(4)	Co–C(8)	2.068(8)
N(1)–C(1)	1.359(5)	Co–C(9)	2.058(8)
N(2)–C(2)	1.341(7)	Co–C(10)	2.074(9)
C(1)–C(2)	1.393(6)	Co–C(11)	2.047(14)
C(2)–C(3)	1.395(7)	Co–C(17)	2.016(25)
C(3)–C(4)	1.350(9)	Co–C(18)	2.003(24)
C(4)–C(5)	1.386(8)	Co–C(19)	1.984(13)
C(5)–C(6)	1.364(8)	Co–C(20)	1.967(12)
C(6)–C(1)	1.403(6)	Co–C(21)	2.023(29)
C(7)–C(8)	1.389(15)	C(7)–C(12)	1.491(17)
C(8)–C(9)	1.458(11)	C(8)–C(13)	1.539(13)
C(9)–C(10)	1.388(12)	C(9)–C(14)	1.568(12)
C(10)–C(11)	1.355(16)	C(10)–C(15)	1.522(13)
C(11)–C(7)	1.482(18)	C(11)–C(16)	1.533(18)
C(17)–C(18)	1.460(30)	C(17)–C(22)	1.497(28)
C(18)–C(19)	1.413(23)	C(18)–C(23)	1.596(28)
C(19)–C(20)	1.444(16)	C(19)–C(24)	1.505(22)
C(20)–C(21)	1.336(24)	C(20)–C(25)	1.524(22)
C(21)–C(17)	1.399(34)	C(21)–C(26)	1.590(33)

TABLE 5

SELECTED BOND ANGLES FOR $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)_2C_6H_4]$ (VII)

N(1)–Co–N(2)	82.2(2)	C(7)–C(8)–C(9)	108.0(8)
C(1)–N(1)–Co	116.8(3)	C(8)–C(9)–C(10)	107.8(7)
C(2)–N(2)–Co	116.9(3)	C(9)–(10)–C(11)	109.5(8)
N(1)–C(1)–C(2)	111.6(4)	C(10)–C(11)–C(7)	109.1(10)
N(2)–C(2)–C(1)	112.5(4)	C(11)–C(7)–C(8)	105.6(10)
0.667 Occupancy [a]			
C(1)–C(2)–C(3)	118.6(5)	C(8)–C(7)–C(12)	126.5(11)
C(2)–C(3)–C(4)	121.3(5)	C(9)–C(8)–C(13)	126.1(9)
C(3)–C(4)–C(5)	120.3(5)	C(10)–C(9)–C(14)	127.4(8)
C(4)–C(5)–C(6)	120.2(5)	C(11)–C(10)–C(15)	124.7(10)
C(5)–C(6)–C(1)	120.0(4)	C(7)–C(11)–C(16)	121.9(11)
C(6)–C(1)–C(2)	119.6(4)		
0.333 Occupancy [a]			
C(17)–C(18)–C(19)	113.0(18)	C(18)–C(17)–C(22)	129.0(21)
C(18)–C(19)–C(20)	102.9(13)	C(19)–C(18)–C(23)	126.0(18)
C(19)–C(20)–C(21)	108.1(14)	C(20)–C(19)–C(24)	131.4(12)
C(20)–C(21)–C(17)	115.5(21)	C(21)–C(20)–C(25)	129.0(15)
C(21)–C(17)–C(18)	99.3(18)	C(17)–C(21)–C(26)	119.6(19)

[a] See Table 2 for atom correspondence.

[η^5-$C_5(CH_3)_5$]Co[(NH)SC$_6$H$_4$] (VIII)

The unit cell consists of four molecules arranged in a head-to-tail fashion as shown in Fig. 3. The molecular structure and atom labelling scheme for VIII are shown in Fig. 4. Unlike VII, no ring disorder is present. A pseudo-mirror plane containing the metallacycle ring also contains C(8) and intersects the C(10)–C(11) bond vector of the CpMe$_5$ ring as shown in Fig. 5. This orientation, IX, is also found in complex VII, but differs from that in related complexes [3–5,7,8,12] wherein the

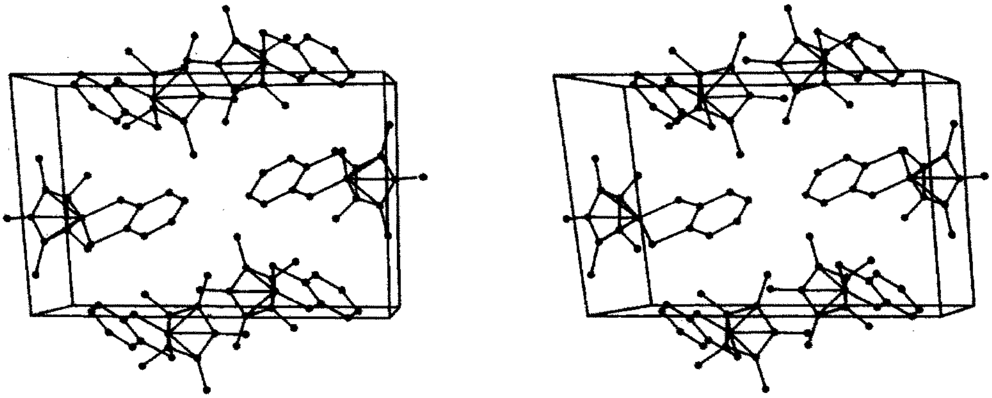


Fig. 3. A stereoview of the unit cell packing of VIII, viewed along the *a*-axis.

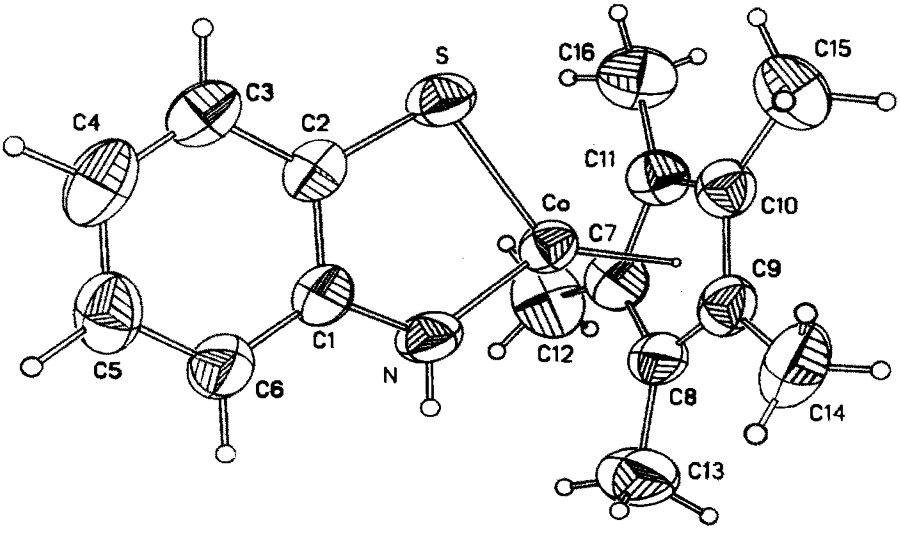
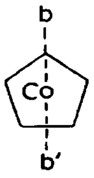
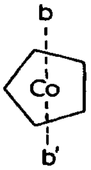


Fig. 4. The molecular structure and atom labelling scheme for [η^5-$C_5(CH_3)_5$]Co[(NH)SC$_6$H$_4$] (VIII) showing the 40% probability thermal ellipsoids.

orientation shown by X exists.



(IX)



(X)

The cyclopentadienyl ring is planar (maximum deviation 0.006 Å) and forms a dihedral angle of 93.1° with the metallacycle fragment. The intra-ring C–C bond distances are close to statistical equivalence as also found in $(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)$ [7], $[\eta^5\text{-}C_5(CH_3)_5]Co(O_2C_6H_4)$ [8], and the diimine complexes [4,12]. This contrasts with $[\eta^5\text{-}C_5(CH_3)_5]Co(CO)_2$ [9] wherein partially localized bonding has been proposed.

The methyl groups attached to C(12), C(13), and C(16) are displaced from the plane of the Cp ring by 0.051, 0.034, and 0.020 Å, respectively, while C(14) and C(15) lie in the plane. C(13) and C(16) are displaced away from the metal while C(12) is displaced toward it. Such methyl group displacements result from the interplay of electronic, steric, and packing effects and are discussed elsewhere [14]. The orientation of the CH_3 groups resembles that in $(\mu\text{-H})(\mu\text{-Cl})\{[\eta^5\text{-}C_5(CH_3)_5]RhCl\}_2$ [15]. One hydrogen atom of each methyl group is *exo* while the other two are *endo* in a tooth/gear arrangment. This orientation minimizes non-bonded interactions.

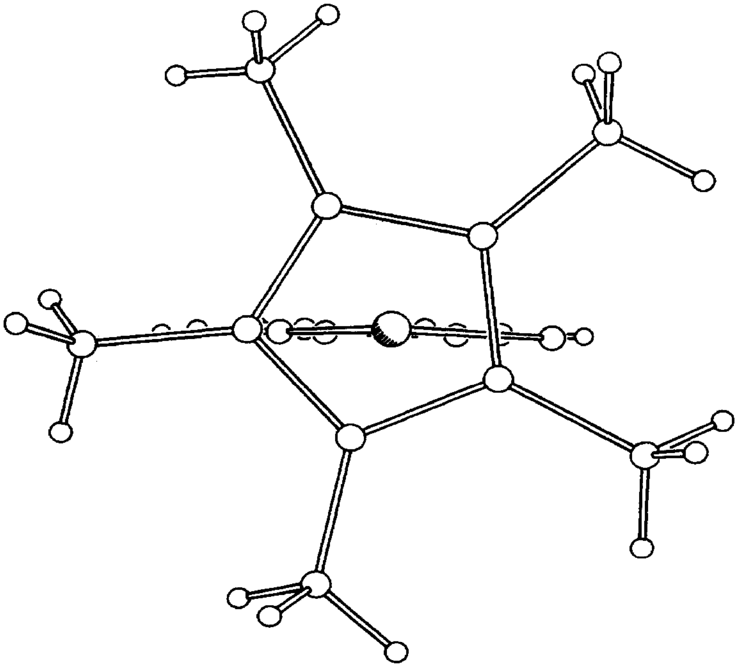


Fig. 5. A view along the Co–CNT axis in VIII showing the orientation of the Cp ring with respect to the metallacycle and the orientation of the CH_3 groups.

The metallacycle ring is planar (maximum deviation 0.016 Å) and nearly coplanar with the phenylene ring (interplanar angle 2.2°). The bonding may be compared to similar fragments · in VII, $(\eta^5\text{-}C_5H_5)Co[(NH)_2C_6H_4]$ [12], $(\eta^5\text{-}C_5H_5)Co\text{-}[(NH)(NC_6F_5)C_6F_4]$ [3], $(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)$ [7], $(\eta^5\text{-}C_5H_5)Co[S_2C_2\text{-}(CN)_2]$ [5], and $(\eta^5\text{-}C_5H_5)Co[S_2C_2(CF_3)_2]$ [16]. The Co–S bond distance in VIII (2.153(1) Å) is longer than in the other dithio chelated complexes by 0.04–0.07 Å, but shorter than the sum of the Co and S covalent radii (2.28 Å) [16]. The C–S bond distance in VIII (1.732(4) Å) is equivalent to that in $(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)$ (1.737(4)

TABLE 6

ATOM COORDINATES ($\times 10^4$) FOR $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)SC_6H_4]$ (VIII)

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)
Co	7606(1)	6384(1)	848(1)	[a]
S	6388(1)	6441(1)	2008(1)	[a]
N	6698(3)	7434(2)	75(3)	[a]
C(1)	5661(4)	7849(3)	360(3)	[a]
C(2)	5373(4)	7419(3)	1337(3)	[a]
C(3)	4311(4)	7787(3)	1678(4)	[a]
C(4)	3553(5)	8547(4)	1054(4)	[a]
C(5)	3854(4)	8985(3)	104(4)	[a]
C(6)	4895(5)	8643(3)	−245(4)	[a]
C(7)	9731(4)	6195(3)	1335(4)	[a]
C(8)	8973(4)	6179(3)	−20(4)	[a]
C(9)	7952(4)	5457(3)	−349(4)	[a]
C(10)	8074(4)	5008(3)	809(4)	[a]
C(11)	9177(4)	5453(3)	1847(4)	[a]
C(12)	10861(5)	6859(4)	2096(7)	[a]
C(13)	9231(6)	6817(4)	−944(6)	[a]
C(14)	6926(5)	5214(4)	−1680(4)	[a]
C(15)	7186(6)	4192(4)	895(5)	[a]
C(16)	9667(5)	5195(3)	3233(4)	[a]
H(1)	6828(36)	7709(25)	−510(33)	41(11)
H(3)	4164(32)	7477(24)	2334(30)	55(10)
H(4)	2850(41)	8829(28)	1279(38)	69(13)
H(5)	3279(38)	9521(24)	−366(33)	65(12)
H(6)	5155(36)	8962(25)	−894(34)	51(11)
H(12a)	11684(52)	6732(32)	1999(43)	83(16)
H(12b)	11142(59)	6948(41)	3056(55)	128(24)
H(12c)	10686(60)	7444(44)	1732(58)	134(24)
H(13a)	9811(56)	6530(33)	−1392(48)	131(19)
H(13b)	9633(48)	7418(35)	−513(45)	130(18)
H(13c)	8525(47)	7018(39)	−1499(48)	140(19)
H(14a)	7268(52)	4713(35)	−1931(45)	93(18)
H(14b)	6707(59)	5706(42)	−2220(53)	118(24)
H(14c)	3913(63)	5065(41)	1678(54)	118(25)
H(15a)	7282(57)	4121(43)	1805(51)	154(21)
H(15b)	7339(55)	3641(38)	469(52)	121(21)
H(15c)	6266(59)	4280(39)	343(50)	111(21)
H(16a)	8910(51)	5034(31)	3530(42)	104(15)
H(16b)	10102(39)	5705(28)	3860(36)	80(13)
H(16c)	10173(53)	4688(36)	3437(46)	133(19)

[a] Anisotropically refined. See Table 7.

Å) [7] and lies between the S–C "single bond" distance of (1.817(5) Å) and the "double bond" distance of 1.71(1) Å [5]. These distances are only approximate guides to bond order. The Co–N bond distance in VIII (1.804(3) Å) is shorter than those in the diimino chelated complexes by 0.03–0.04 Å, while the C–N bond distance is 0.01–0.03 Å longer [3,12]. The Co–N–C angle (123.1(3)°) is larger than that in VII or the other diimino complexes above (116–118°), but this is very likely a

TABLE 7

ANISOTROPIC TEMPERATURE FACTORS (Å^2 ×10^3) FOR $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)SC_6H_4]$ (VIII)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	37(1)	47(1)	42(1)	1(1)	19(1)	3(1)
S	50(1)	59(1)	52(1)	5(1)	30(1)	1(1)
N	51(2)	59(2)	49(2)	10(2)	32(2)	10(2)
C(1)	38(2)	50(2)	42(2)	−1(2)	15(2)	0(2)
C(2)	34(2)	52(2)	42(2)	−9(2)	15(2)	−5(2)
C(3)	50(3)	71(3)	56(3)	−3(2)	29(2)	2(2)
C(4)	45(3)	89(4)	72(3)	−18(3)	28(2)	7(3)
C(5)	48(3)	66(3)	62(3)	−2(2)	15(2)	19(2)
C(6)	63(3)	62(3)	54(3)	4(2)	29(2)	16(3)
C(7)	38(2)	57(3)	68(3)	4(2)	25(2)	5(2)
C(8)	58(3)	53(3)	63(3)	13(2)	41(2)	22(2)
C(9)	51(3)	51(3)	48(2)	−1(2)	22(2)	14(2)
C(10)	47(2)	49(2)	50(2)	1(2)	20(2)	7(2)
C(11)	44(2)	52(3)	44(2)	5(2)	13(2)	4(2)
C(12)	42(2)	74(4)	115(5)	−6(4)	24(3)	−8(3)
C(13)	93(4)	88(4)	107(4)	38(4)	74(4)	35(4)
C(14)	86(4)	88(4)	57(3)	−18(3)	21(3)	23(3)
C(15)	66(4)	58(3)	82(4)	−1(3)	21(3)	−8(3)
C(16)	68(3)	85(4)	49(3)	11(3)	9(2)	2(3)

[a] The anisotropic temperature factor exponent takes the form, $-2\pi^2(h^2a^{*2}U_{11}^2 + k^2b^{*2}U_{22}^2 + \ldots + 2hka^*b^*U_{12}^2 + \ldots)$.

TABLE 8

SELECTED BOND DISTANCES (Å) FOR $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)SC_6H_4]$ (VIII)

Co–S	2.153(1)	Co–C(7)	2.041(4)
Co–N	1.804(3)	Co–C(8)	2.035(5)
C(2)–S	1.732(4)	Co–C(9)	2.035(5)
C(1)–N	1.367(6)	Co–C(10)	2.038(4)
C(1)–C(2)	1.402(6)	Co–C(11)	2.050(4)
C(2)–C(3)	1.399(6)	Co(7)–C(8)	1.421(6)
C(3)–C(4)	1.363(6)	C(8)–C(9)	1.414(6)
C(4)–C(5)	1.388(8)	C(9)–C(10)	1.427(6)
C(5)–C(6)	1.371(7)	C(10)–C(11)	1.418(5)
C(6)–C(1)	1.398(6)	C(11)–C(7)	1.435(6)
		C(7)–C(12)	1.481(7)
		C(8)–C(13)	1.495(8)
		C(9)–C(14)	1.497(5)
		C(10)–C(15)	1.510(7)
		C(11)–C(16)	1.497(6)

TABLE 9

SELECTED ANGLES (deg.) FOR [η^5-$C_5(CH_3)_5$]Co[(NH)SC_6H_4] (VIII)

N–Co–S	87.4(1)	C(7)–C(8)–C(9)	108.9(4)
C(2)–S–Co	98.9(2)	C(8)–C(9)–C(10)	107.8(3)
C(1)–N–Co	123.1(3)	C(9)–C(10)–C(11)	108.0(4)
C(2)–C(1)–N	115.4(3)	C(10)–C(11)–C(7)	108.1(3)
C(1)–C(2)–S	115.2(3)	C(11)–C(7)–C(8)	107.1(3)
C(1)–C(2)–C(3)	119.3(3)		
C(2)–C(3)–C(4)	120.2(5)	C(8)–C(7)–C(12)	127.1(5)
C(3)–C(4)–C(5)	120.6(5)	C(9)–C(8)–C(13)	125.7(4)
C(4)–C(5)–C(6)	120.4(4)	C(10)–C(9)–C(14)	126.5(4)
C(5)–C(6)–C(1)	119.9(5)	C(11)–C(10)–C(15)	126.6(4)
C(6)–C(1)–C(2)	119.5(3)	C(7)–C(11)–C(16)	126.2(3)
C(11)–C(7)–C(12)	125.7(5)		
C(7)–C(8)–C(13)	125.3(4)		
C(8)–C(9)–C(14)	125.7(4)		
C(9)–C(10)–C(15)	125.3(3)		
C(10)–C(11)–C(16)	125.7(4)		

result of the need to accommodate the sulfur atom in the metallacycle. As might be expected, the N–Co–S angle (87.4(1) Å) lies between that in VII (82.2(2)°) and (η^5-C_5H_5)Co($S_2C_6H_4$) [7] (92.3(1)°).

The C–C bond distances in the phenylene ring shows the long-short pattern consistent with III. The C–S bonds in (η^5-C_5H_5)Co[$S_2C_2(CN)_2$] have also been described in this manner [5].

Discussion

Molecular packing

Molecules of VII and VIII pack in a head-to-tail fashion similar to that in other complexes of this type whose structures are known. These include (η^5-C_5H_5)Co-[$(NH)_2C_6H_4$] [12], (η^5-C_5H_5)Co[(NH)(NC_6F_5)C_6F_4] [3], (η^5-C_5H_5)Co($S_2C_6H_4$) [7], [η^5-$C_5(CH_3)_5$]Co($O_2C_6H_4$) [8], (η^5-C_5H_5)Co[$S_2C_2(CN)_2$] [5], (η^5-C_5H_5)-Co[$S_2C_2(CF_3)_2$] [16], and [η^5-$C_5(CH_3)_5$]Rh($O_2C_6H_4$) [6]. While it is unlikely that this motif is the only possible one, it makes intuitive sense that space is best filled in this arrangement while also providing an antiparallel alignment of molecular dipole moments.

Cyclopentadienyl

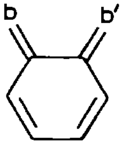
Two rotomers of η^5-C_5R_5 have emerged. Complexes VII and VIII in this study adopt rotomer IX while X is found in [η^5-$C_5(CH_3)_5$]Co($O_2C_6H_4$) [8], (η^5-C_5H_5)Co($S_2C_6H_4$) [7], (η^5-C_5H_5)Co[(NH)(NR)C_6R_4'], $R = C_6F_5$, $R' = H$, F [3,12] and [η^5-$C_5(CH_3)_5$]$Co(CO)_2$ [9]. There are no important intra- or intermolecular contacts that appear to produce the difference. The energy barrier between IX and X is expected to be very small (1–2 kcal mol^{-1}) causing us to conclude that these orientational differences are unimportant in the bonding of these molecules.

The small differences (0.03 Å) in the intra-ring C–C bond distances can be assigned to allyl-ene (V) and diene (VI) distortions that result from the lifting of the degeneracy in the e_1'' MO of Cp by the twofold symmetry of the metallacycle fragment. Such distortions surely exist in these molecules [9–11,17], but the effect is small.

Metallacycle

Co–b and b–C bond distances in these complexes are shorter than the sum of the covalent radii. These observations are inconsistent with IV as an adequate description of the electron distribution. ^{59}Co NQR coupling constant data for these complexes, which suggest that the Co–b bond contains little π-character in the ground state, are inconsistent with both II and IV [1,2]. If II were the most appropriate description, differences in the metallacycle structure should be witnessed when η^5-C_5H_5 is replaced by η^5-$C_5(CH_3)_5$ because the mixing of the π MO's of the Cp ring with those of the metallacycle should perturb the bond lengths in the metallacyle. This comparison can be made with VII and $(\eta^5\text{-}C_5H_5)Co[(NH)_2C_6H_4]$ [12] where it is found that no differences occur within experimental error. Thus, II seems to contribute less than III, although some π-character is undoubtedly present in the Co–b bond.

The phenylene fragment contains long-short C–C bond distances consistent with partial redistribution of electron density in the π-system shown in the extreme by XI. The metallacycle alone would resemble III. All of the *o*-phenylene chelated complexes discussed in this paper show this electron distribution, as do other metal complexes containing these types of ligands.



(XI)

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