The structure of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_4Me\text{-}4)]$

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(Received October 27, 1993)

Abstract

The structure of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_4Me\text{-}4)]$ has been determined by a X-ray diffraction study and shown to be similar to that of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$. The μ_3-CNC_6H_4Me-4 ligand acts as a 2e donor, but back bonding to it results in bending at N, differentiation of its two C-N π^* orbitals, and formation of a 'pseudo' mirror-plane in the molecule. The consequent distortions within the $CCo_3(S)$ 'trigonal bipyramid' are significant and suggest that a $[\{Co(\eta\text{-}C_5H_5)(t\text{-}CNC_6H_4Me\text{-}4)\}\{Co_2(\eta\text{-}C_5H_5)_2(\mu_2\text{-}S)\}]$ mesomer contributes towards an overall description of the bonding within the molecule.

Key words: Cobalt; Isocyanide; Cyclopentadienyl; Crystal structure

1. Introduction

The compounds $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ were the first series of complexes to be prepared that contained CNR ligands as μ_3 two electron donors (R = alkyl or aryl) [1,2]. The structures of two in which R = alkyl were determined by X-ray diffraction, R = C_6H_{11} [1] and Et[2]. The structure of a complex in which R = aryl has now been determined in order to see if structural variations reflected the differences between the ν(CN) stretching frequencies [2] of *ca.* 1650 cm^{-1} when R = alkyl and 1550 cm^{-1} when R = aryl.

2. Experimental details

The complex $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_4\text{-}Me\text{-}4)]$ was prepared as described elsewhere [2] and a single crystal grown from a tetrahydrofuran-hexane mixture at −15°C.

Crystal data are given in Table 1, heavy atom coordinates in Table 2, selected bond lengths and angles in Table 3, and least squares planes in Table 4. Complete lists of bond lengths and bond angles, anisotropic displacement parameters for the heavy atoms, and hydrogen atom coordinates and isotropic thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre.

The structure was solved by direct methods, SHELX86 [3], and refined by full-matrix least squares using SHELX-93 [4]. Data were corrected for Lorentz and polarisation effects but not for absorption. One of the cyclopentadienyl rings, C(19) to C(23), was disordered over two positions with site occupancies of 0.5 each. Except for those on the disordered ring, hydrogen atoms were included in calculated positions with common, fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. All calculations were performed on a VAX 6610 computer. The ORTEP program was used to obtain the drawings [5].

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0022-328X/94/$7.00
SSDI 0022-328X(93)24303-M

3. Results and discussion

The structure is illustrated in Fig. 1. It is similar to that found for [$Co_3(\eta$-$C_5H_5)_3(\mu_3$-S)(μ_3-CNEt)], and is based on a Co_3 triangle capped on one face by a μ_3-S ligand and on the other by a μ_3-C of CNC_6H_4Me-4. A η-C_5H_5 ligand is coordinated to each cobalt atom so that their centroids lie almost in the Co_3 plane; the ring coordinated to Co(2) is disordered equally over two positions about the metal to ring-centroid axis. The molecule is a 48 e system with bond lengths and angles comparable to those in [$Co_3(\eta$-$C_5R_5)_3(\mu_3$-Y)(μ_3-CX)] and related derivatives (CX, Y = CO, NH [6]; CO, $CONH_2$ [6]; CO, O [7]; CO, S [8]; CS, S [9].

However, the $Co_3(\mu_3$-S)(μ_3-C) moiety does not possess a 3-fold axis of symmetry. Instead, there is almost a mirror plane defined by S(1), Co(2), C(1), N(1) and C(2) which lies at an angle of 90.4° to the Co(1)–Co(2)–Co(3) plane and bisects the Co(1)–Co(3) bond only 0.024 Å from its midpoint. The distances Co(1)–

TABLE 1. Crystal data for [$Co_3(\eta$-$C_5H_5)_3(\mu_3$-S)(μ_3-CNC_6H_4Me-4)]

Crystal Size (mm)	0.28×0.32×0.39
Formula	$C_{23}H_{22}Co_3NS$
M (a.m.u.)	521.27
Crystal system	Orthorhombic
Space group	*Pbca* No. 61
a (Å)	14.932(4)
b (Å)	15.851(3)
c (Å)	17.516(1)
U (Å³)	4145.8(14)
Z	8
D_c(g cm^{-3})	1.670
Diffractometer	Enraf-Nonius CAD4F
Temperature	293(2) K
Wavelength	0.71069 Å
Absorption coefficient	2.482 mm^{-1}
F(000)	2112
θ Range for data collection	2.21° to 25.99°
Index ranges	$-4 < h < 16$, $-4 < k < 17$, $-8 < l < 19$
Reflections collected	4030
Independent reflections	3883 [*R*(int) = 0.0283]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3883/0/250
Goodness-of-fit on F^2	1.008
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0538$, $wR_2 = 0.1403$
R indices (all data)	$R_1 = 0.0865$, $wR_2 = 0.1531$
Largest positive/ negative peak (e/Å³)	1.116/−0.823

$R_1 = [\Sigma| |F_o| - |F_c| |]/\Sigma|F_o|$
$wR_2 = [[\Sigma_w(|F_o - F_c|)^2]/\Sigma_w(|F_o|)^2]]^{1/2}$
$w = q/[(\sigma F_o)^2 + (a^*P)^2 + b^*P + d + e^* \sin(\theta)]$
Goodness-of-fit $= [\Sigma_w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{parameters})]^{1/2}$

TABLE 2. Atomic coordinates (×10⁴) and equivalent displacement parameters (Å² ×10³) for [$Co_3(\eta$-$C_5H_5)_3(\mu_3$-S)(μ_3-CNC_6H_4Me-4)]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	U_{eq}
Co(1)	173(1)	4004(1)	2008(1)	36(1)
Co(2)	820(1)	4755(1)	3085(1)	40(1)
Co(3)	1369(1)	5104(1)	1815(1)	34(1)
S(1)	1531(1)	3917(1)	2349(1)	43(1)
N(1)	−432(3)	5800(3)	2216(2)	38(1)
C(1)	143(3)	5234(3)	2235(3)	37(1)
C(2)	−898(3)	6155(3)	1600(3)	34(1)
C(3)	−1481(4)	6818(3)	1771(3)	41(1)
C(4)	−1973(4)	7192(3)	1188(3)	50(1)
C(5)	−1891(4)	6936(4)	444(4)	54(2)
C(6)	−1293(4)	6288(4)	291(3)	49(1)
C(7)	−807(3)	5907(3)	854(3)	39(1)
C(8)	−2439(6)	7349(5)	−176(4)	85(2)
C(9)	1624(4)	5590(4)	726(3)	52(2)
C(10)	1357(4)	6245(4)	1219(3)	48(1)
C(11)	1976(4)	6286(4)	1820(3)	49(1)
C(12)	2618(4)	5651(4)	1706(3)	48(1)
C(13)	2397(4)	5231(3)	1022(3)	49(1)
C(14)	−1134(4)	3903(4)	1614(5)	66(2)
C(15)	−1045(4)	3472(5)	2307(4)	67(2)
C(16)	−395(5)	2828(4)	2161(5)	69(2)
C(17)	−121(5)	2912(4)	1417(5)	72(2)
C(18)	−581(5)	3580(4)	1092(4)	65(2)
C(19)	1589(10)	5128(11)	4029(8)	45(4)
C(20)	955(9)	5767(6)	3882(5)	30(2)
C(21)	66(8)	5406(8)	3922(5)	30(2)
C(22)	120(11)	4501(12)	4119(8)	52(3)
C(23)	1074(14)	4369(9)	4211(7)	50(3)
C(119)	1405(17)	5384(16)	3982(12)	89(7)
C(120)	502(16)	5597(11)	3906(9)	72(4)
C(121)	−2(11)	4870(14)	4023(9)	63(4)
C(122)	590(13)	4233(8)	4156(7)	48(3)
C(123)	1456(11)	4516(10)	4131(8)	51(4)

C(19)–C(23) disordered with C(119)–C(123).

TABLE 3. Selected bond lengths and angles for [$Co_3(\eta$-$C_5H_5)_3(\mu_3$-S)(μ_3-CNC_6H_4Me-4)] with estimated standard deviations in parentheses

Bond lengths (Å)			
Co(1)–Co(2)	2.430(1)	Co(1)–S(1)	2.118(2)
Co(1)–Co(3)	2.518(1)	Co(2)–S(1)	2.133(2)
Co(2)–Co(3)	2.435(1)	Co(3)–S(1)	2.115(2)
Co(1)–C(1)	1.989(5)	C(1)–N(1)	1.243(6)
Co(2)–C(1)	1.953(5)	C(2)–N(1)	1.401(6)
Co(3)–C(1)	1.984(5)		
Bond angles (°)			
Co(1)–Co(2)–Co(3)	62.36(3)	Co(1)–S(1)–Co(3)	69.74(5)
Co(1)–Co(3)–Co(2)	58.73(3)	Co(1)–S(1)–Co(3)	73.02(5)
Co(2)–Co(1)–Co(3)	58.91(3)	Co(1)–S(1)–Co(3)	69.93(5)
Co(1)–C(1)–Co(2)	76.1(2)	C(1)–N(1)–C(2)	130.8(5)
Co(1)–C(1)–Co(3)	78.7(2)	N(1)–C(2)–C(3)	116.5(5)
Co(2)–C(1)–Co(3)	76.4(2)	N(1)–C(2)–C(7)	124.7(5)

TABLE 4. Equations of least squares planes given in the form $lx + my + nz - p = 0$ where x, y, and z are atomic coordinates. The relevant atoms and their deviations from the planes are given in the square parentheses

Plane 1. $0.715x + 0.689y - 0.119z - 5.420 = 0$	[Co(2), −0.006; S(1), −0.004; C(1), 0.017; N(1), 0.008; C(2), −0.014]
Plane 2. $0.733x + 0.666y - 0.137z - 5.142 = 0$	[C(1), −0.005; N(1), 0.020; C(2), 0.004; C(3), −0.014; C(4), −0.002; C(5), 0.001; C(6), −0.008; C(7), −0.007; C(8), 0.010]
Plane 3. $-0.705x + 0.705y - 0.084z - 3.996 = 0$	[Co(1), 0; Co(2), 0; Co(3), 0]

Co(2) and Co(2)–Co(3) are identical within experimental error, and significantly shorter than Co(1)–Co(3). The distances Co(1)–S(1) and Co(3)–S(1) are also identical and SHORTER than Co(2)–S(1); at the same time the distances Co(1)–C(1) and Co(3)–C(1) are identical and LONGER than Co(2)–C(1), but for these bond lengths the errors are larger and the differences only just significant. However, similar variations were found for $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$ [2], so we are confident that they are real.

The distortions are probably due to the back-bonding from the Co_3S moiety into the μ_3-CNC_6H_4Me-4 ligand. This is bent at N so that the plane defined by N, C(2) and the remainder of the arene ring, C(3)–C(9), (Table 4) lies at only 1.94° to the pseudo-mirror plane mentioned above that bisects the Co(1)–Co(3) bond. Although this increases the π-acceptor ability of the isocyanide ligand and, incidentally, the σ-bonding to Co(2), the loss of C–N–R axial symmetry means that the two C–N π^* orbitals are not degenerate and may

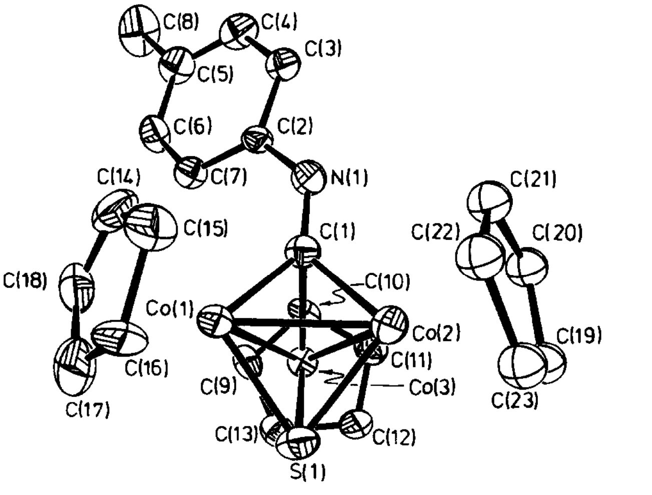

Fig. 1. Structure and atom labelling of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_4Me\text{-}4)]$.

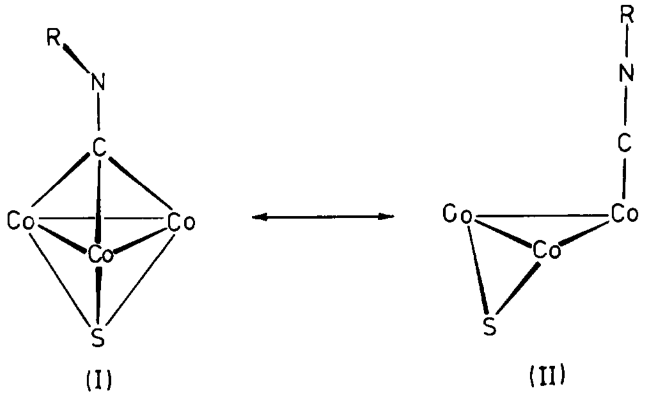

Fig. 2. Some resonance forms of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$. η^5-Cyclopentadienyl ligands have been omitted for the sake of clarity.

not be equally effective acceptors [10]. The orientation of the aryl group is such as to allow conjugation of one of the C–N π^* orbitals (π_z^* in ref. 10) with the aromatic π^* orbitals, which would be expected to result in CNC_6H_4Me-4 becoming a better acceptor and the distortion of the Co_3 triangle to a greater extent than CNEt, as is observed (*cf.* ref. 2). The distortions are consistent with contributions of resonance form (II) (Fig. 2) towards an overall description of the bonding within the molecule, which is dominated by form (I). Distortion of the $Co_3(\mu_3\text{-}Y)(\mu_3\text{-}CX)$ core are not observed in $[Co_3(\eta\text{-}C_5Me_5)_3(\mu_3\text{-}NH)(\mu_3\text{-}CO)]$ despite the presence of a crystallographically-imposed mirror plane [6]; the π^* orbitals of μ_3-CO cannot lose their degeneracy and the 3-fold axial symmetry of the $Co_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)$ moiety is retained.

The angle of bending at N (130.7°) and the C–N bond length (1.243(7) Å) are virtually identical with those in $[Co_3(\eta_3\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$ {130.6° and 1.231(8) Å}, although the Co–C distances are somewhat shorter [2]. The lower ν(CN) frequency and hence the implied greater π-acceptor ability of the μ_3-aryl isocyanide is not reflected in either the C(1)–N bond length or in the bending at N. It seems to be reflected in the rather short C(2)–N distance, which implies multiple bond character and which is found in other aryl isocyanide complexes such as $[Fe_2(\eta\text{-}C_5H_5)_2(CNPh)_4]$ [11].

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