O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1		
E_g	2	–1	0	0	2	2	0	–1	2	0		$(2z^2 - x^2 - y^2, \sqrt{3}\ (x^2 - y^2))$
T_{1g}	3	0	–1	1	–1	3	1	0	–1	–1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	–1	–1	3	–1	0	–1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	–1	–1	1	–1	1	–1	–1	1		
E_u	2	–1	0	0	2	–2	0	1	–2	0		
T_{1u}	3	0	–1	1	–1	–3	–1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	–1	–1	–3	1	0	1	–1		

T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2 - x^2 - y^2,\ \sqrt{3}\ (x^2 - y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	(xy, xz, yz)

Tetrakis(1-norbornyl)cobalt, a Low Spin Tetrahedral Complex of a First Row Transition Metal

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The crystal structure of tetrakis(1-norbornyl)cobalt (**1**) was determined and, together with magnetic susceptibility measurements, establishes (**1**) as the first example of a low spin tetrahedral complex of a first row transition metal and as the only structurally characterized cobalt(IV)–alkyl complex.

The splitting of the five degenerate d-orbitals of a transition metal ion in a tetrahedral ligand field is not generally big enough to enforce pairing of its electrons. Indeed, no low spin tetrahedral complex of an ion of the first transition series has been shown to exist prior to this work.[1] In 1972 Bower and Tennent[2] reported a series of tetrakis(norbornyl) complexes [M(1-norbornyl)$_4$], M = Ti, V, Cr, Mn, Fe, Co, Zr, Hf, which exhibited magnetic moments consistent with low spin configurations for the iron and cobalt compounds. However, none of these complexes was structurally characterized. This is all the more disappointing since tetrakis(1-norbornyl)cobalt (**1**) is also the only thermally stable alkyl complex of cobalt in its unusually high formal oxidation state IV.[3a] Herein we report the results of a crystal structure determination and measurements of the magnetic susceptibility of (**1**).

A suitable crystal of (**1**) was isolated from a diethyl ether solution of its anion [PPN]$^+$[Co(1-norbornyl)$_4$]$^-$ [PPN = (Ph$_3$P)$_2$N], which had been cooled to −35 °C for 1 month.† It is conceivable that this unintended slow oxidation minimized the problem of crystal disorder, which has apparently thwarted previous attempts to determine the structure of any one of these tetrakis(norbornyl) complexes.[4] In this case the structure was solved using standard procedures and the refinement converged to a final *R*-factor of 0.071.‡ Careful inspection of the structure, however, revealed some unrealistic bond distances and angles within the norbornyl ligands. We attributed this to threefold rotational disorder about the Co–C bonds of these groups. Since there was little doubt about the actual structural features of the norbornyl skeleton, and one of

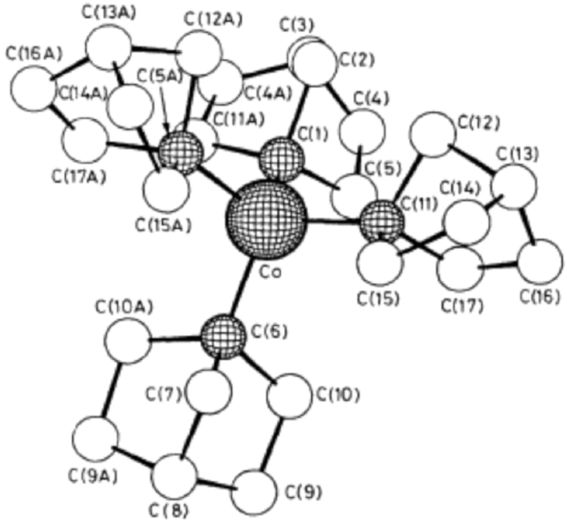

Figure 1. The molecular structure of tetrakis(1-norbornyl)cobalt, looking down the crystallographic mirror plane. The shaded atoms constitute the tetrahedral inner co-ordination sphere of the complex. These atoms are not disordered. The open circles depict the best model for the whole molecule resulting from a constrained refinement (see text). Selected bond distances (Å) and angles (°); results from an unconstrained refinement and in square brackets, from a constrained refinement. Co–C(1) 1.930(21) [1.910(25)], Co–C(6) 1.928(19) [1.911(23)], Co–C(11) 1.912(23) [1.930(27)]; C(1)–Co–C(6) 114.4(12) [113.4(15)], C(1)–Co–C(11) 106.5(11) [106.9(12)], C(6)–Co–C(11) 108.4(12) [109.0(13)], C(11)–Co–C(11A) 112.7(8) [111.6(15)].

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† The oxidation of [Co(1-norbornyl)$_4$]$^-$ is a facile and reversible reaction which may be accomplished using O_2 as an oxidant. The chemistry of this compound will be described in a separate publication.

‡ *Crystal data:* $C_{28}H_{44}Co$, $M = 439.59$, orthorhombic, $a = 11.948(3)$, $b = 10.104(2)$, $c = 9.805(3)$ Å, $U = 1183.75(50)$ Å^3, $\lambda(\text{Cu-}K_\alpha) = 1.54178$ Å, space group $Pmn2_1$, $D_c = 1.233$ g cm^{-3}, $Z = 2$, red-brown crystal from Et$_2$O, 0.35 × 0.35 × 0.40 mm, $\mu(\text{Cu-}K_\alpha) = 56.1$ cm^{-1}. 1820 Data were collected on a Syntex P2$_1$ diffractometer using a θ–2θ scan method, 681 had $I > 3\sigma(I)$ and 146 parameters were refined; $R = 0.089$, $R_w = 0.107$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.