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
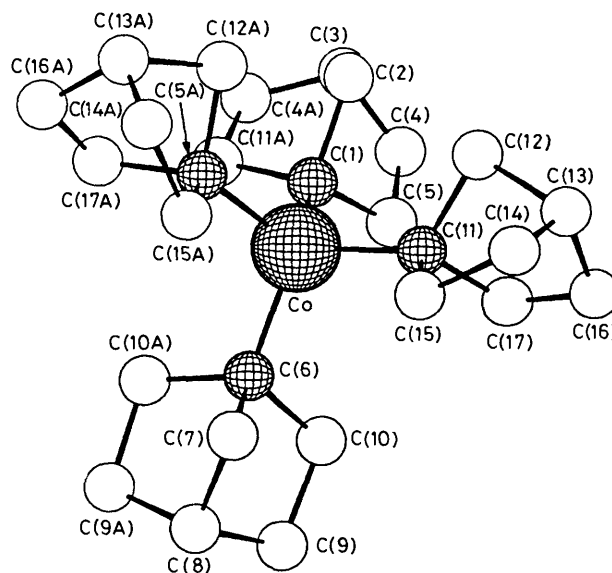
Figure 1. The molecular structure of tetrakis(1-norbornyl)cobalt, looking down the crystallographic mirror plane. The shaded atoms constitute the tetrahedral inner co-ordination sphere of the complex. These atoms are not disordered. The open circles depict the best model for the whole molecule resulting 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 disordered conformations predominated, we decided to impose a corresponding constraint on the refinement. Starting with experimentally determined bond distances and angles of the norbornyl group[5] as constraints, we used the program CRYSTALS[6] to refine the structure of the major contributor according to a method described by Waser.[7] This procedure results in a slightly higher R-factor (0.089) but yields a chemically sensible model for the ligands. In any case, the point of interest is the inner co-ordination sphere of the cobalt atom, which is not affected by the method of refinement. The following discussion is based on the results of this constrained refinement.

The molecular structure of (1) (Figure 1) features a slightly distorted tetrahedron as the co-ordination environment of cobalt. The molecule has crystallographic C_s symmetry only [the Co atom and carbon atoms C(1), C(2), C(3), C(6), C(7), and C(8) lie on the mirror plane], but the four cobalt bonded carbon atoms approximate the pseudo D_{2d} symmetry of a tetragonally compressed tetrahedron. The Co–C bond distances are equal within the error of the measurement and average 1.92 Å. These distances are not sensitive to the refinement method. For comparison, cobalt–carbon bond distances range between 1.93 and 2.22 Å in 6-co-ordinate Co^{III}–alkyl complexes, many of which have been structurally characterized.[3b] The short metal–carbon bond distance in (1) probably reflects both the lesser steric demand of the 4-co-ordinate molecule and the high formal oxidation state of the cobalt centre.

Cobalt in its oxidation state IV has a d^5 configuration and is thus expected to have five unpaired electrons in a high spin complex and only one unpaired electron in an unprecedented low spin tetrahedral complex. The effective magnetic moment of (1) had been determined previously by an n.m.r. method.[2] The reported value of 2.00 μ_B is consistent with only one unpaired electron. Given the unusual nature of this result we have reinvestigated the magnetic susceptibility of solid (1) using a Faraday balance. The magnetic susceptibility of (1) was measured in the temperature interval 1.7—299 K. The complex is paramagnetic and the data may be fitted with a Curie–Weiss expression.[8] The effective magnetic moment of (1) at 299 K is 1.89 μ_B, in close agreement with the previously reported value.

Thus tetrakis(1-norbornyl)cobalt is the first unambiguously characterized example of a low spin tetrahedral complex of a first row transition metal. With its single unpaired electron in the antibonding t$_2$ orbital set it should be subject to a

Jahn–Teller distortion. We hesitate, however, to attribute to this the slight tetragonal compression observed in the crystal structure. This particular distortion, unlike the expected tetragonal elongation,[9] is not suited for removing completely the electronic degeneracy of the e^{4}t$_2$^{1} configuration of (1). Other possible explanations for the distortion are crystal packing forces and steric interactions between adjacent norbornyl ligands. (1) is also of interest as the first structurally characterized Co^{IV}–alkyl complex. Organometallic compounds of cobalt in this unusually high oxidation state have been generated in solution and characterized spectroscopically, but their high reactivity has prevented isolation.[10] The stability of (1) suggests that the Co^{IV}–C bond is not inherently unstable, e.g. with respect to homolytic dissociation.

References

1 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' John Wiley and Sons, New York, 1980, p. 647.

2 B. K. Bower and H. G. Tennent, *J. Am. Chem. Soc.*, 1972, **94**, 2512.

3 G. Wilkinson, F. G. A. Stone, and E. W. Abel, 'Comprehensive Organometallic Chemistry,' vol. 5, Pergamon Press, Oxford, 1982, (a) p. 153; (b) p. 100.

4 H. B. Abrahamson, K. L. Brandenburg, B. Lucero, M. E. Marti, and E. Dennis, *Organometallics*, 1984, **3**, 1379.

5 R. A. Alden, J. Kraut, and T. G. Traylor, *J. Am. Chem. Soc.*, 1968, **90**, 74.

6 CRYSTALS is a crystallographic program written by D. J. Watkin and J. R. Carruthers, Chemical Crystallography Laboratory, University of Oxford, 1981.

7 J. Waser, *Acta Crystallogr.*, 1963, **16**, 1091.

8 R. L. Carlin, 'Magnetochemistry,' Springer-Verlag, Berlin, 1986, pp. 5—12. The data were fit to the expression $\chi_M = C/(T - \theta)$ + TIP. $C = 0.447$ e.m.u. K/mol, $\theta = 0.7$ K, TIP = 1.35×10^{-4} e.m.u./mol.

9 B. K. Bower, M. Findlay, and J. C. W. Chien, *Inorg. Chem.*, 1974, **13**, 759.

10 For a recent review of the organometallic chemistry of Co^{IV} see: M. E. Vol'Pin, I. Ya. Levitin, A. L. Sigan, and A. T. Nikitaev, *J. Organomet. Chem.*, 1985, **279**, 263.