

Exchange of Bridging and Terminal Hydrides in [Co(terpy)(H₂BH₂)] †

Donald J. Wink and N. John Cooper *

Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, MA 02138, U.S.A.

Dynamic n.m.r. studies have shown that the barrier to exchange of the bridging and terminal hydride ligands in [Co(terpy)(H₂BH₂)] (terpy = 2,2':6',2''-terpyridyl) is 11.1 (±0.1) kcal mol⁻¹, the highest value measured to date for a bidentate H₂BH₂⁻ complex. Solutions of the complex are diamagnetic within the limits of the n.m.r. method of measuring susceptibilities.

The tetrahydroborato-ligand typically bonds to transition-metal complexes by using two¹ (occasionally one² or three³) of its hydrides as bridging ligands. These bridging hydrides can be distinguished spectroscopically from the terminal boron hydrides by means of the characteristic boron-hydride stretching frequencies,^{1a,4} but in most cases the barrier to exchange between bridging and terminal sites is low and only exchange-averaged absorptions can be observed in the ¹H n.m.r. spectra.^{1a} There are three reports of exceptions to this, in which distinct bridging and terminal hydride resonances were observed at ambient temperatures,⁵⁻⁷ and two cases in which it has been possible to measure the exchange barrier in bidentate tetrahydroborato-*H,H'* (H₂BH₂) complexes by dynamic n.m.r.^{8,9} The exchange barrier in some tridentate tetrahydroborato-*H,H',H''* (H₃BH) complexes has been measured in solution¹⁰ and in the solid state.¹¹ Slow bridge-terminal exchange has been observed in one Sc¹¹¹-H₂BH₂ complex by ¹¹B n.m.r.¹² We wish to report the determination of the exchange barrier in a third bidentate H₂BH₂ complex, [Co(terpy)(H₂BH₂)] (terpy = 2,2':6',2''-terpyridyl),⁴ which exhibits the highest barrier measured to date for any tetrahydroborato-complex.

Experimental

General.—All manipulations of [Co(terpy)(H₂BH₂)] were carried out under dry nitrogen. 1,2-Dimethoxyethane (dme) was distilled from sodium benzophenone ketyl before use. Ethylene glycol benzyl methyl ether (ebme) was prepared by the literature method,¹³ and distilled under vacuum from 3 Å molecular sieves before use. [²H₆]Acetone (99.95%, Merck) was used as purchased. NaBH₄ was gently flame dried (450 K) under vacuum. [Co(terpy)(H₂BH₂)] was prepared as described previously.⁴ Samples for magnetic studies were purified by recrystallization from dme at 220 K in the presence of at least an equimolar quantity of NaBH₄.

N.M.R. Studies.—All spectra were recorded under vacuum in sealed tubes. Typical dynamic n.m.r. samples in degassed [²H₆]acetone (ca. 50% of the saturated concentration) were stored at 77 K to inhibit the slow 298 K decomposition observed in this solvent. Spectra were recorded on a Bruker WM-300 spectrometer at 300 MHz for ¹H and 96 MHz for ¹¹B. Variable-temperature spectra were calibrated using the difference in chemical shift between the ¹H resonances of the CH₃ and OH groups of methanol:¹⁴ precise results required the operation of the ¹¹B decoupler during calibration. Boron-11 spectra were calibrated externally using the BF₃·Et₂O resonance at δ 0 p.p.m.

† (2,2':6',2''-Terpyridyl)(tetrahydroborato-*H,H'*)cobalt(I).

Non-S.I. units employed: cal = 4.184 J, B.M. = 0.927 × 10⁻²³ A m², χ_{g.s.} = χ_{s.l.} × 10⁶/4π.

Solution Susceptibility Study.—An almost saturated solution of [Co(terpy)(H₂BH₂)] was prepared by adding 2 cm³ of ebme saturated with NaBH₄ (≈0.001 g cm⁻³, 0.03 mol dm⁻³) to [Co(terpy)(H₂BH₂)] (0.036 g, 0.118 mmol). The sample was sealed in an n.m.r. tube with a capillary of ebme containing dissolved O₂. At 300 MHz the methoxy resonance of the capillary was observed to be 2.4 Hz downfield of the bulk solvent absorption at 298 K. Under the same conditions the capillary resonance was 2.3 Hz downfield of the resonance of pure deoxygenated ebme, so that the net paramagnetic shift produced by the Co complex was 0.1 (±0.3) Hz. Equation (i),

$$\chi_s = \frac{3\Delta v}{4\pi m v} + \chi_0 + \chi_0(d_0 - d_s/m) \quad (i)$$

appropriate for a longitudinal magnet/sample geometry, was used to interpret the data.^{15, ‡}

Results

At ambient temperatures the ¹H n.m.r. spectrum of [Co(terpy)(H₂BH₂)] exhibits a single broad resonance arising from the tetrahydroborato-ligand.⁴ The failure to observe coupling to ¹¹B (*I* = $\frac{3}{2}$, 81%) indicates rapid relaxation of the ¹¹B nucleus *via* coupling of the quadrupole moment to the fluctuating field gradients at the nucleus produced by molecular tumbling in solution. Marks^{1a,16} and Beall and Bushweller¹⁷ have pointed out that such 'thermal decoupling' can explain the loss of ¹¹B coupling in spectra of transition-metal tetrahydroborates as the temperature is lowered. In the present case, although ¹¹B splitting is not observed in the ambient ¹H spectrum, ¹H coupling is observed in the ¹¹B spectrum [a 1 : 4 : 6 : 4 : 1 quintet at δ 12.94 with *J*(¹¹B-H) = 80 ± 5 Hz]. Boron-11 irradiation allows the effect of the residual ¹¹B coupling on the ¹H spectrum to be observed: *w*₃ for the singlet decreased from 630 to 370 Hz with a decoupler input of 5.2 W. Since no further change was seen up to 6.0 W, 5.2 W was used in decoupled experiments.

Diffraction studies have established that the BH₄⁻ ligand in [Co(terpy)(H₂BH₂)] binds through two bridging hydrides,⁴ and the observation of a single broad BH₄⁻ resonance in the ¹H-¹¹B} n.m.r. spectrum suggests that there is rapid exchange between the bridging and terminal hydrides and that the signals are not far above coalescence at ambient temperatures. This has been confirmed by variable-temperature ¹H-¹¹B} n.m.r. studies. As the temperature is lowered the singlet collapses and two new resonances of equal intensity appear at

‡ χ_s and χ₀ = gram magnetic susceptibilities of sample and solvent respectively, *v* = spectrometer frequency, *d*_s and *d*₀ = densities (g cm⁻³) of solution and solvent respectively, *m* = mass of sample per cm³ of solution.

Table. Barrier to exchange of bridging and terminal hydrides in [Co(terpy)(H₂BH₂)] at temperatures *T*: (a) as determined from $w_{\frac{1}{2}}$ for the bridging hydride resonance below coalescence and (b) as determined from $w_{\frac{1}{2}}$ of the averaged BH₄⁻ resonance above coalescence. See text for assumptions

<i>T</i> /K	$w_{\frac{1}{2}}$ /Hz	<i>k</i> /Hz	ΔG^{\ddagger} /kcal mol ⁻¹
(a)			
213 ± 1	39 ± 1	—	—
218 ± 1	41 ± 1	—	—
223 ± 1	56 ± 1	54 ± 4	11.15 ± 0.06
228 ± 1	73 ± 1	107 ± 4	11.11 ± 0.05
233 ± 1	99 ± 1	189 ± 4	11.10 ± 0.05
237 ± 1	126 ± 2	396 ± 7	10.94 ± 0.05
244 ± 1	191 ± 5	478 ± 16	11.19 ± 0.05
249 ± 1	295 ± 8	804 ± 25	11.17 ± 0.05
254 ± 1	400 ± 15	1 135 ± 47	11.23 ± 0.05
(b)			
295 ± 1	630 ± 30	20 900 ± 1 100	11.43 ± 0.04
303 ± 1	370 ± 15	37 300 ± 2 000	11.41 ± 0.04
315 ± 1	246 ± 10	61 600 ± 4 300	11.57 ± 0.05

δ -9.97 and 1.73. The characteristic high-field shift of hydrides bonded to transition metal atoms¹⁸ indicates that the resonance at δ -9.97 can be assigned to the bridging hydrides while that at δ 1.73 can be assigned to the terminal hydrides. These new assignments are consistent with those for other bidentate H₂BH₂ complexes,⁵⁻⁹ two of which are supported by decoupling studies.^{5,6} The chemical shift of the terminal hydrides is somewhat higher than in previous examples, which fall in the range δ 4.3-7 (cf. δ 4.0 for the terminal hydrides of diborane⁸). The temperature dependent behaviour is fully reversible on warming.

The barrier to exchange has been determined from the linewidth of the averaged BH₄⁻ resonance above coalescence and of the bridging hydride resonance below coalescence (Table).^{*} The high-temperature range was limited to 315 K, when decomposition became rapid in this solvent. Low-temperature data were recorded from 254 K to the point where further changes became negligible (213 K). The linewidth at the lower limit was assumed to be the linewidth in the absence of exchange, $w_{\frac{1}{2}}^0$, and was used to calculate T_2^{eff} from the relation¹⁹ $T_2^{\text{eff}} = (\pi w_{\frac{1}{2}}^0)^{-1}$. This value was then used to calculate the rate of exchange, *k*, below coalescence using the slow exchange limit approximation.¹⁹ The rate of exchange above coalescence was calculated in the fast exchange approximation¹⁹ using the value of $w_{\frac{1}{2}}^0$ obtained below coalescence. The free energies of activation for exchange (ΔG^{\ddagger}) were calculated using the Eyring equation,²⁰ taking the transmission coefficient $\kappa = 1$ as is usual in dynamic n.m.r. studies.^{19a} In view of the susceptibility studies below, it is important to note that the observed linewidths were insensitive to the history and condition of the samples; only extensive solvent promoted reaction at temperatures above ambient produced significant increases in the linewidth of resonances. The quoted uncertainties † were calculated as in ref. 19b, equation 111.

Our previous report indicated that solid samples of [Co(terpy)(H₂BH₂)] exhibited weak paramagnetism;⁴ since this could have had a significant effect on the n.m.r. spectra of the

* As a consequence of the limited solubility of the complex the absorptions of the terminal hydrides are obscured by the solvent absorption at some temperatures, even using 99.95% deuteriated acetone, and were therefore not used for linewidth measurements. At 213 K, where both resonances can be observed, the bridging and terminal resonances have similar contours.

molecule, we have re-examined the magnetic behaviour of the compound. Measurement of the susceptibility of solid samples by the Evans modification of the Gouy method again indicated a low level of paramagnetism, but the values obtained varied from sample to sample and could be reduced below a level corresponding to $\mu_{\text{eff.}} = 0.8$ B.M. (at 298 K), the sensitivity limit of the available facilities, by careful recrystallization of the compound from dme containing NaBH₄. These results suggested that the observed paramagnetism was due to paramagnetic or ferromagnetic contamination, although all the samples consisted of well developed crystals, and had similar i.r. spectra to samples which gave satisfactory combustion analyses.

To circumvent this solid-state ambiguity we determined the susceptibility in solution in the presence of excess NaBH₄ using the n.m.r. method. The limited solubility of [Co(terpy)(H₂BH₂)] in most inert solvents required the use of PhCH₂OCH₂CH₂OCH₃ (ebme; an aromatic solvent and also a glycol ether) which is the best solvent discovered for the complex. It is also a poor but adequate solvent for NaBH₄. The Co complex is stable for weeks in ebme containing NaBH₄ under vacuum.

These experiments provide no evidence for intrinsic paramagnetism in [Co(terpy)(H₂BH₂)]. The methoxy resonances of ebme were essentially unshifted in a 0.06 mol dm⁻³ solution of the complex, a result which is consistent with the diamagnetic susceptibility of the complex being almost exactly equal to that of the solvent,‡ with a negligible density difference between solvent and solution. We conclude that the solid-state measurements indicate small quantities of paramagnetic or ferromagnetic impurities, and since the linewidths of the BH₄⁻ resonances measured in the dynamic n.m.r. experiments were independent of the history of the sample of the Co complex used, while susceptibility studies were very sensitive to sample history, we further conclude that these impurities do not play a significant role in determining the linewidths of the BH₄⁻ resonances.

Discussion

The barrier to exchange of the bridging and terminal hydrides in [Co(terpy)(H₂BH₂)] is the largest measured to date for any tetrahydroborato-complex, although the exchange barriers in the complexes for which distinct bridging and terminal hydride resonances are observed at ambient temperatures⁵⁻⁷ are probably larger. The previous largest value measured was also for a bidentate H₂BH₂ complex {10.0 ± 0.2 kcal mol⁻¹ in [N(PPh₃)₂][Mo(CO)₄(H₂BH₂)]⁹}, but ΔG^{\ddagger} is significantly lower in the only other bidentate H₂BH₂ complex in which it has been measured {7.6 ± 0.3 kcal mol⁻¹ in [V(η -C₅H₅)₂(H₂BH₂)]⁸}, and an even lower upper-limit of 4.9 kcal mol⁻¹ has been estimated for the barrier in the H₂BH₂ complex [Hf(η -C₅H₅Me)₂(H₂BH₂)₂].²³ The values reported for tridentate H₃BH complexes are within the range reported for bidentate H₂BH₂ complexes.^{10,11}

The establishment of the exchange barrier in [Co(terpy)(H₂BH₂)] widens the range of measured tetrahydroborato-

† The uncertainties do not take account of the potential inaccuracy involved in assuming T_2^{eff} to be temperature independent, and hence do not allow for the possibility of temperature-dependent ⁵⁹Co quadrupolar broadening of the bridging hydride resonances. This is probably not a serious source of error at low temperatures, given the similarity in linewidth (27 Hz) of the bridging (Co-bonded) and terminal hydrides at 213 K.

‡ Values predicted on the basis of literature values for 2,2'-bipyridyl,²¹ pyridine,²² benzene,²² and dimethoxymethane²² as modified by the use of Pascal's constants:²¹ ebme, χ_{H} = 0.651 × 10⁻⁶ c.g.s. units; [Co(terpy)(H₂BH₂)], χ_{H} = 0.645 × 10⁻⁶ c.g.s. units.

exchange barriers and confirms that they are highly variable, but the origin of variations within this range remains unclear. It would seem probable that the variations reflect underlying structural differences, but the paucity of precise (neutron) structural data for BH_4^- complexes^{2,3d,4,23,24} precludes critical examination of structural criteria at this time.

Acknowledgements

We thank the National Science Foundation for support of our research program. These studies were made possible by the availability of a Bruker WM300 n.m.r. spectrometer purchased with N. S. F. funds. N. J. C. is a Fellow of the Alfred P. Sloan Foundation, 1982–1984.

References

- (a) T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263; (b) R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1.
- F. Takusagawa, A. Fumagalli, T. F. Koetzle, S. G. Shore, T. Schmitkons, A. V. Fratini, K. W. Morse, C.-Y. Wei, and R. Bau, *J. Am. Chem. Soc.*, 1981, **103**, 5165.
- (a) V. P. Spridonov and G. I. Mamaeva, *J. Struct. Chem. (Engl. Transl.)*, 1969, **10**, 120; (b) K. N. Semenenko, E. B. Lobkovskii, and A. E. Shumakov, *Zh. Strukt. Khim.*, 1977, **18**, 389; (c) V. Plato and K. Hedberg, *Inorg. Chem.*, 1971, **10**, 590; (d) E. R. Bernstein, W. C. Hamilton, S. J. Keiderling, S. J. Laplaca, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, 1972, **11**, 3009.
- E. J. Corey, N. J. Cooper, W. M. Canning, W. N. Lipscomb, and T. F. Koetzle, *Inorg. Chem.*, 1982, **21**, 192.
- H. D. Empsall, E. Mentzer, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1975, 861; H. D. Empsall, E. M. Hyde, E. Mentzer, B. L. Shaw, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1976, 2069.
- T. J. Mazanec, J. B. Letts, and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1982, 356; J. B. Letts, T. J. Mazanec, and D. W. Meek, *J. Am. Chem. Soc.*, 1982, **104**, 3898.
- R. H. Crabtree and A. J. Pearman, *J. Organomet. Chem.*, 1978, **157**, 335.
- T. J. Marks and W. J. Kennelly, *J. Am. Chem. Soc.*, 1975, **97**, 1439.
- S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Grynkewich, T. J. Marks, D. L. Tipton, and B. R. Whittlesey, *J. Am. Chem. Soc.*, 1977, **99**, 7154.
- T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, 1975, **97**, 27.
- I.-S. Chuang, T. J. Marks, W. J. Kennelly, and J. R. Kolb, *J. Am. Chem. Soc.*, 1977, **99**, 7539.
- M. F. Lappert, A. Singh, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1983, 206.
- E. M. Van Duzee and H. Adkins, *J. Am. Chem. Soc.*, 1935, **57**, 147.
- A. L. Van Geet, *Anal. Chem.*, 1968, **40**, 2227.
- D. F. Evans, *J. Chem. Soc.*, 1959, 2003; K. D. Bartle, D. W. Jones, and S. Maricic, *Croat. Chem. Acta*, 1968, **40**, 227; D. H. Lire and S. I. Chan, *Anal. Chem.*, 1970, **42**, 791.
- T. J. Marks and L. A. Shimp, *J. Am. Chem. Soc.*, 1972, **94**, 1542.
- H. Beall and C. H. Bushweller, *Chem. Rev.*, 1973, **73**, 465 and refs. therein.
- A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747, 4583.
- (a) G. Binsch, *Top. Stereochem.*, 1968, **3**, 97; (b) G. Binsch, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds., L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, ch. 3.
- S. Glasstone, K. J. Laidler, and H. Eyring, 'The Theory of Rate Processes,' McGraw-Hill, New York, 1941, p. 195.
- L. N. Mulay, 'Magnetic Susceptibility,' John Wiley, New York, 1963, ch. IID.
- 'Handbook of Chemistry and Physics,' 58th edn., CRC Press, Cleveland, 1977, p. E127.
- P. L. Johnson, S. A. Cohen, T. J. Marks, and J. M. Williams, *J. Am. Chem. Soc.*, 1978, **100**, 2709.
- R. W. Bronch, I.-S. Chuang, T. J. Marks, and J. M. Williams, *Inorg. Chem.*, 1983, **22**, 1081.

Received 23rd August 1983; Paper 3/1487