Dynamic Nuclear Magnetic Resonance Studies of Complexes of 1,2-Bis(benzylthio)ethane with Chromium, Molybdenum, and Tungsten Carbonyl Complexes

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Band-shape fitting studies have been made for the n.m.r. spectra of the benzylic methylene protons of the complexes $[M(CO)_4(bbse)]$ [where M = Cr, Mo, or W; (bbse) = 1,2-bis(benzylthio)ethane]. These studies show that the coalescence phenomenon observed in the temperature-dependent n.m.r. spectra results not from reversal of the chelate ring but from inversion of configuration about the ligand sulphur atoms. Thermodynamic activation parameters for this latter process are reported.

THERE has recently been controversy as to the cause of the coalescence phenomenon observed in the temperature-dependent ^1H n.m.r. spectra of metal complexes of 1,2-bis(alkylchalcogeno)ethanes. One of us (R. J. C.) has attributed this phenomenon to inversion of configuration at the ligand atoms,[1,2] whereas the other two (G. H. and R. C. M.) have suggested that it arises from conformational changes occurring in the five-membered chelate ring.[3] With the advent of computer programs which allow the simulation of complex spin spectra under exchange conditions,[4] in principle it is possible to elucidate which process is responsible for the temperature dependence of an n.m.r. spectrum. This may be achieved by detailed analysis of possible exchange mechanisms and comparison, over a range of exchange rates, of the simulated spectra based on these mechanisms with the experimental spectrum at various temperatures. For complexes of 1,2-bis(alkylchalcogeno)-ethanes, depending on the individual circumstances, such spectral analysis may be made for either the chelate-ring methylene protons or for the protons of suitable alkyl groups. The preceding paper reported the results of spectral analysis for the chelate-ring methylene protons of complexes of 1,2-bis(isopropylseleno)ethane (bise), whereas this paper reports analogous results for the benzylic methylene protons of complexes of 1,2-bis(benzylthio)ethane (bbse). Both studies show conclusively that the coalescence phenomenon observed in the spectra of these complexes results from configurational inversion at the ligand atoms and not from reversal of the five-membered chelate ring.

RESULTS AND DISCUSSION

The complexes of 1,2-bis(benzylthio)ethane were readily prepared in reasonable yield by displacement of the bidentate hydrocarbon ligand from (bicyclo[2.2.1]-heptadiene)tetracarbonylmetal [equation (1)]. The complexes have good solubility in organic solvents and gave adequately resolved ^1H n.m.r. spectra over the necessary

$$[M(C_7H_8)(CO)] + bbse \longrightarrow [M(CO)_4(bbse)] \quad (1)$$

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[1] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.

[2] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, 1974, 207.

[3] R. Donaldson, G. Hunter, and R. C. Massey, *J.C.S. Dalton*, 1974, 288.

[4] G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 1304.

temperature range. The 90-MHz ^1H n.m.r. spectra of $[Cr(CO)_4(bbse)]$, $[Mo(CO)_4(bbse)]$, and $[W(CO)_4(bbse)]$ in $CDCl_3$ were very similar and the methylene-proton region of the 'frozen-out' spectrum of the molybdenum complex is shown in Figure 1. The spectrum of the benzylic methylene protons consisted of two partially overlapping AB quartets, the less intense (s) being centred at τ 5.92 and the more intense (a) at τ 6.13. The chelate-ring methylene-proton spectrum, although not as well resolved, was very similar to those of the complexes of 1,2-bis(isopropylseleno)ethane,[5] and consisted of an apparent broad singlet at τ 7.33 and a more intense, poorly resolved, multiplet centred at τ 7.38. As the temperature of the sample was increased the spectra began to coalesce, such that at room temperature the methylene-proton spectrum consisted of two singlets. At 320 K, the benzylic methylene singlet had effectively regained its natural linewidth which was approximately half that of the 'frozen-out' components of the AB quartet at 210 K, implying that the relaxation time for these protons is temperature dependent.

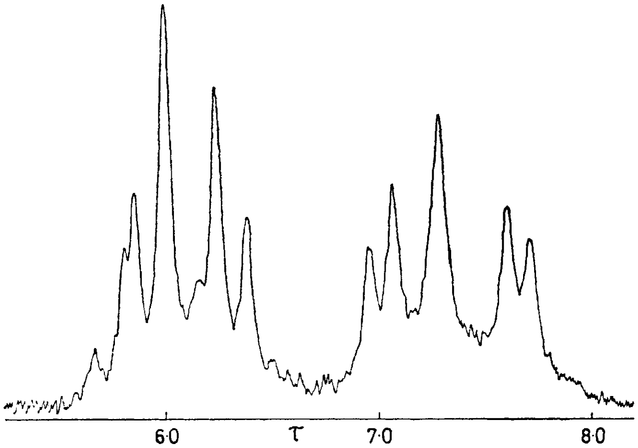


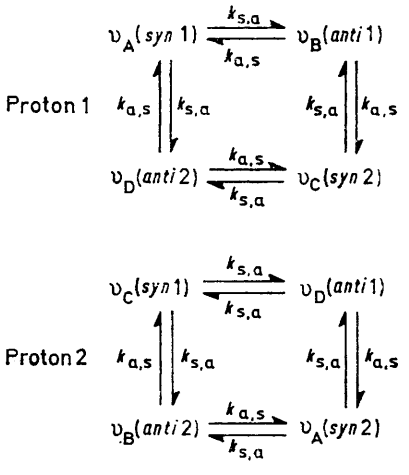
FIGURE 1 90 MHz N.m.r. methylene–proton spectrum of $[Mo(CO)_4(bbse)]$ in $CDCl_3$ at 210 K

A tetrahedral environment, with the fourth position presumably occupied by a lone pair of electrons, about co-ordinated chalcogen atoms has been well established by X-ray crystallographic studies.[6,7] In principle, the complexes $[M(CO)_4(bbse)]$ can exist in two isomeric forms with the benzyl groups either projected on the same (*syn*) or opposite (*anti*) sides of the chelate ring. The similarity of the chelate-ring methylene-proton spectra of these complexes to those of 1,2-bis(isopropylseleno)ethane complexes strongly suggest that configurational inversion at the ligand atoms is the process responsible for the coalescence phenomenon observed in the spectra. If this is so, then in the 'frozen-out' spectrum the more intense benzylic AB quartet (a) can be attributed to the conformationally time-averaged *anti* isomer, and the less intense AB quartet (s) to the conformationally time-averaged *syn* isomer.

As the benzylic methylene groups are bonded to chiral sulphur atoms, their geminal methylene protons will be intrinsically non-equivalent. The net effect of configurational inversion is to exchange the environments of these geminal protons, such that for each conformation in the configurational inversion cycle there is an enantiomeric conformation in which these protons are interchanged. Therefore, on rapid configurational inversion, the intrinsic non-equivalence will no longer affect the appearance of the spectrum so that an A_2 singlet will result.

That the coalescence phenomenon is attributable to isomeric interconversion was confirmed by band-shape fitting studies. The program DNMR2[8] was used to simulate the benzylic methylene-proton spectra at various rates of exchange and the input parameters used for such simulations are recorded in Table 1. All the coupling constants and chemical-shift differences for each AB quartet, and the relative populations of the isomers, were temperature invariant in the 'frozen-out' spectra and were assumed to remain constant in the regions of intermediate and fast exchange. However, as previously mentioned, the relaxation time for these protons was temperature dependent; the values of T_2 chosen for the spectral simulations were those which, within the upper and lower limits found in the fast-exchange and 'frozen-out' spectra, gave the best fit with the experimental spectra.

The spectra were then simulated on the basis of the two benzylic methylene protons exchanging between four different environments as follows:



Here ν_A and ν_C represent the chemical shifts of the intrinsically non-equivalent environments of the *syn* isomer, and ν_B and ν_D the intrinsically non-equivalent environments of the *anti* isomer. The simulated spectra, together with the appropriate values of $k_{a,s}$ which give the best agreement with the experimental benzylic

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[5] G. Hunter and R. C. Massey, preceding paper.

[6] H. J. Whitfield, *J. Chem. Soc.* (*A*), 1970, 113.

[7] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 501.

[8] G. Binsch and D. A. Kleier, Program 140, Quantum Chemistry Program Exchange, Indiana University.

methylene spectrum, are shown in Figure 2 for $[Mo(CO)_4(bbse)]$. We consider that the good fit of simulated with experimental spectra in the regions of intermediate and fast exchange confirms that configurational inversion about the ligand atoms causes the observed coalescence phenomenon. Attempted band-shape simulation by simple exchange of quartet AB (a) with quartet AB (s) by either of the two possible ways, AC $\rightleftharpoons$ BD or AC $\rightleftharpoons$ DB, did not give the correct spectrum in the regions of intermediate and fast exchange, thus confirming that reversal of the five-membered chelate ring was not the process causing the coalescence phenomenon.

TABLE 1

Input parameters for the simulation of the benzylic methylene-proton spectra

Complex	$\frac{T}{K}$	Solvent	P_s	$\Delta\nu_{AB,(s)}$	$J_{AB,(s)}$	P_A	$\Delta\nu_{AB,(a)}$	$J_{AB,(a)}$	$\frac{T_2}{s}$
				Hz			Hz		
$[Cr(CO)_4(bbse)]$	225	$CDCl_3$	0.26	25.2	−13.5	0.74	31.2	−13.5	0.10
$[Mo(CO)_4(bbse)]$	210	$CDCl_3$	0.24	30.1	−13.5	0.76	33.4	−13.5	0.07
$[W(CO)_4(bbse)]$	220	$CDCl_3$	0.28	28.7	−13.5	0.72	30.2	−14.0	0.06

TABLE 2

Thermodynamic parameters (in kJ mol^{-1}) for the configurational inversion process of the complexes

Complex	Solvent	ΔG_{300}(a,s)	$E^‡$(s)	$\Delta H_{300}^‡$(s)	$\Delta G_{300}^‡$(s)	$E^‡$(a)	$\Delta H_{300}^‡$(a)	$\Delta G_{300}^‡$(a)
$[Cr(CO)_4(bbse)]$	$CDCl_3$	2.61 ± 0.13	72.5 ± 17.1	70.0 ± 17.1	45.5 ± 3.1	64.7 ± 17.1	62.2 ± 17.1	51.9 ± 3.1
$[Mo(CO)_4(bbse)]$	$CDCl_3$	2.88 ± 0.14	62.1 ± 13.2	59.6 ± 13.2	43.5 ± 3.8	63.9 ± 13.2	61.4 ± 13.2	45.8 ± 3.8
$[W(CO)_4(bbse)]$	$CDCl_3$	2.35 ± 0.13	66.4 ± 9.5	63.9 ± 9.5	50.1 ± 2.0	65.5 ± 9.5	63.0 ± 9.5	52.9 ± 2.0

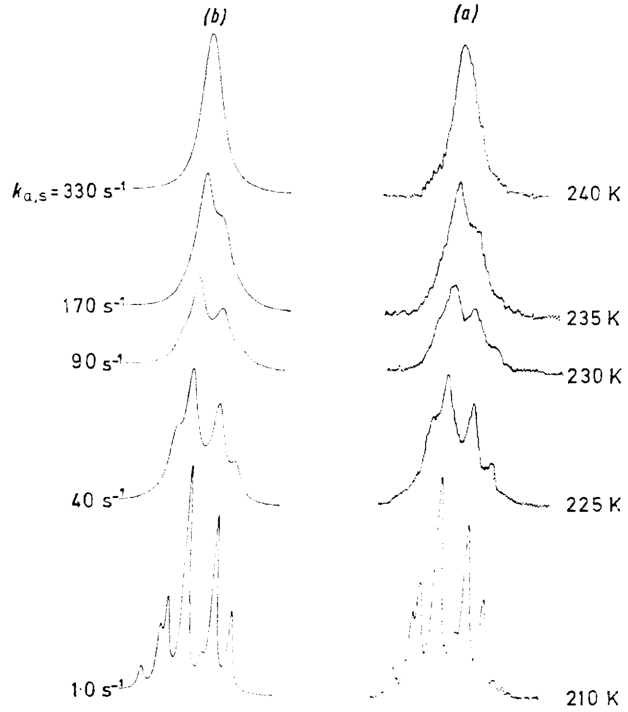

FIGURE 2 90-MHz N.m.r. benzylic methylene–proton spectra of $[Mo(CO)_4(bbse)]$ in $CDCl_3$: (a) observed; (b) simulated

Acceptable Arrhenius plots of $\log_{10}k$ against $1/T$ were obtained and thermodynamic activation parameters calculated from these plots are recorded in Table 2. It is of interest to note that the values for these parameters are *ca.* 20% lower than those for the corresponding selenium ligand complexes.[5]

EXPERIMENTAL

1,2-*Bis*(*benzylthio*)*ethane Complexes with Metal Tetracarbonyls*.—These were prepared by heating 1,2-bis(benzylthio)ethane under reflux with the appropriate (bicyclo-[2.2.1]heptadiene)tetracarbonylmetal in n-heptane, under nitrogen, for 30 min. On cooling, and after evaporation of the solvent, the residue was recrystallised from chloroform–hexane to give the required complexes (Found: C, 54.9; H, 4.2. Calc. for $C_{20}H_{18}CrO_4S_2$: C, 54.8; H, 4.1. Found: C, 50.1; H, 3.8. Calc. for $C_{20}H_{18}MoO_4S_2$: C, 49.8; H, 3.7. Found: C, 41.9; H, 3.5. $C_{20}H_{18}O_4S_2W$ requires C, 42.1; H, 3.2%). Molecular-weight and molar-conductance measurements showed that the complexes are neutral monomeric species in chloroform.

N.M.R. Spectra.—90-MHz Hydrogen-1 n.m.r. spectra were obtained using a Bruker HX90 spectrometer fitted with a variable-temperature probe. Temperatures were measured with a thermocouple mounted in the probe which was found to be accurate to ±1 °C by calibration with methanol and ethylene glycol using the formulae of Van Geet.[9]

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[9] A. L. Van Geet, *Analyt. Chem.*, 1968, **40**, 2227.