1,4-Diselenantetracarbonyl Complexes of Chromium, Molybdenum, or Tungsten: Chelate Complexes of a Cyclic Ligand in the Boat Conformation

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The preparation and ^{1}H n.m.r. spectra are reported for the new complexes $LM(CO)_4$ where L is 1,4-diselenan and M is Cr, Mo, or W. The complexes are neutral monomeric species with a ligand in the boat conformation acting in a chelating mode and an analogy is drawn between these complexes and norbornane. The AA′BB′ n.m.r. spectra of the complexes have been analysed and chemical shifts and coupling constants are reported.

THE replacement of a methylene group in an alicyclic ring by a heteroatom usually does not have a profound effect on the conformational properties of the system. For example, it is well established that, like cyclohexane, 1,4-dioxan,[1] 1,4-dithian,[2-4] 1,4-diselenan,[5] and piperazine,[1] exist in chair conformations and that these molecules are even more flexible than cyclohexane itself. An indication of their flexibility is given by the temperatures at which coalescence phenomena occur in the n.m.r. spectra; cyclohexane 206 K,[6] 1,4-dioxan $<$ 169 K,[7] 1,4-dithian $<$ 153 K,[8] and 1,4-diselenan 170 K.[9] It is also well established [10] that the inversion of cyclohexane occurs *via* an intermediate twist-boat conformation and there seems little reason to suggest that the heterocyclic molecules do otherwise than invert by a similar mechanism. Conse-

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[1] M. Davis and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181.

[2] H. J. Dothie, *Acta Cryst.*, 1953, **6**, 804.

[3] R. E. Marsh, *Acta Cryst.*, 1955, **8**, 91.

[4] K. Hayasaki, *J. Chem. Soc. Japan*, 1960, **81**, 1645.

[5] R. E. Marsh and J. D. McCullough, *J. Amer. Chem. Soc.*, 1951, **73**, 1106.

[6] F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, 1962, **84**, 386.

[7] E. Caspi, T. A. Wittstruck, and D. M. Piatak, *J. Org. Chem.*, 1962, **27**, 3183.

[8] F. Lautenschlager and G. F. Wright, *Canad. J. Chem.*, 1963, **41**, 1972.

[9] G. Hunter and R. C. Massey, unpublished observation.

[10] See, *e.g.* F. A. Bovey, ' Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, p. 192.

quently, the ready formation of metal chelate complexes containing these ligands in a boat conformation might be expected.

Although a number of reports suggest otherwise, there is, in fact, little conclusive evidence for the existence of such chelate complexes. Barnes[11] has recently discounted evidence that 1,4-dioxan can chelate, and the preliminary structural report[12] of a $PdCl_2$ chelate complex of *NN'*-dimethylpiperazine has not so far been substantiated. Hendra[13] has reported Pd^{II} and Pt^{II} halide complexes of 1,4-diselenan (L) with stoicheiometry LMX_2 for which i.r. spectral evidence suggested that the molecule existed either as a dinuclear species with two bridging ligands in the chair conformation, or as a mononuclear species with a ligand in the boat conformation acting in a chelating mode. Of the two structures it was considered that the former was the more likely. However, Rice and Walton,[14] as a result of Raman spectral work, have suggested that the latter structure is the more probable for the analogous 1,4-dithian complexes.

As part of our studies of metal complexes formed with organoselenium ligands we now report complexes of the type $LM(CO)_4$, where M is chromium, molybdenum, or tungsten. These complexes were readily prepared by heating n-heptane solutions of 1,4-diselenan with bicyclo[2.2.1]heptadienetetracarbonylmetal and were obtained as well formed yellow-green crystals which were very soluble in acetone and chloroform. Molecular weight and conductance measurements in these solvents (Table 1) showed the complexes to be neutral monomeric species. The monomeric nature of these complexes indicated that 1,4-diselenan was acting either in a chelating mode or as a monodentate ligand with the sixth co-ordination position about the metal occupied by a solvent molecule.

TABLE 1

Molecular weights and molar conductances for the complexes in $(CH_3)_2CO$

Complex	*M*	Λ/Ω^{-1} cm^2 (for mM solution)
$LCr(CO)_4$	379	0·9
$LMo(CO)_4$	435	0·3
$LW(CO)_4$	471	0·8

The well resolved 90 MHz n.m.r. spectra of all the complexes were very similar whether obtained in $CDCl_3$ or $(CD_3)_2CO$ solutions and that of the molybdenum complex is shown in Figure 1. Except for slight changes in the positions of the complete spectra, all were temperature-invariant over the range 200—330 K. At least sixteen lines were resolved in each spectrum, which in every case was perfectly symmetrical about its mid-point and therefore analysed as an AA'BB' multiplet. The spectral analyses were obtained by use of the LAOCOON 3 program[15] and the chemical shifts and coupling constants are recorded in Table 2. That the values calculated for the coupling constants retain a consistent pattern and adequately reproduce non-first-order spectra at the several, quite widely different, internal chemical shifts on going from $LCr(CO)_4$ to $LW(CO)_4$ shows that they are almost certainly correct.

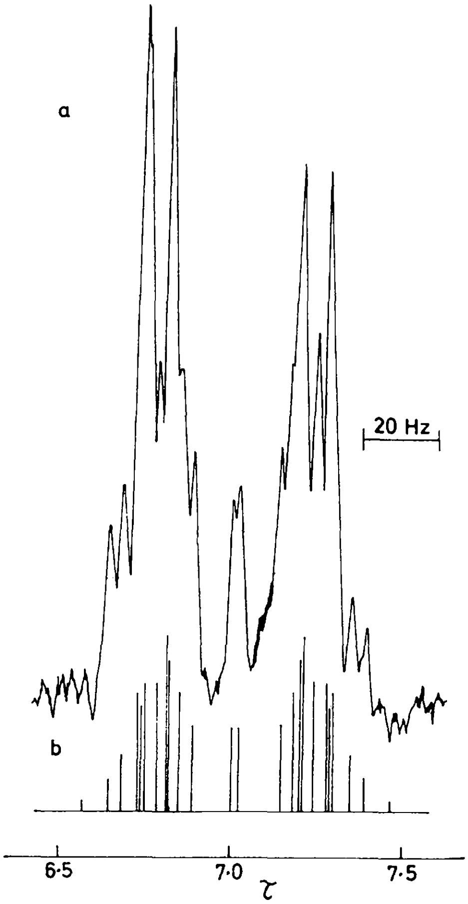

FIGURE 1 90 MHz N.m.r. spectrum of $LMo(CO)_4$ in $(CD_3)_2CO$: a, observed; b, calculated

TABLE 2

90 MHz N.m.r. data (ν, *J* in Hz) for the complexes

Complex	$\Delta\nu_{AB}$	J_{AB}	$J_{A'B'}$	$J_{AA'}$	$J_{BB'}$	$J_{AB'}$	$J_{A'B}$
$LCr(CO)_4$	30·4	−11·4	−11·4	12·3	8·4	3·4	3·4
$LMo(CO)_4$	42·1	−12·4	−12·4	10·9	7·1	5·7	5·7
$LW(CO)_4$	62·6	−11·4	−11·4	12·6	9·3	5·4	5·4

DISCUSSION

1,4-Diselenan co-ordinated as a monodentate ligand would no longer have two equi-energy chair conformations

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[11] J. C. Barnes and C. S. Dundan, *Inorg. Chim. Acta*, 1973, **7**, 404.

[12] O. Hassel and B. F. Pedersen, *Proc. Chem. Soc.*, 1959, 394.

[13] P. J. Hendra and N. Sadasivan, *J. Chem. Soc.*, 1965, 2063.

[14] D. A. Rice and R. A. Walton, *Spectrochim. Acta*, 1971, 279.

[15] A. A. Bothner-by and S. Castellano, Program 111, Quantum Chemistry Program Exchange, Indiana University, 1973.

as the metal atom may occupy either an axial or an equatorial ring position as shown in Figure 2. Slow interconversion of the two chair forms would give n.m.r. spectra for the complexes consisting of two overlapping ABCD multiplets. It is unlikely that there would be equal populations (P_{I} and P_{II}) for the two conformations and even with rapid interconversion, an ABCD spectrum would be observed, the chemical shifts being given by equations (1)—(4) and the vicinal couplings by equations (5)—(8). In principle an ABCD spectrum should be

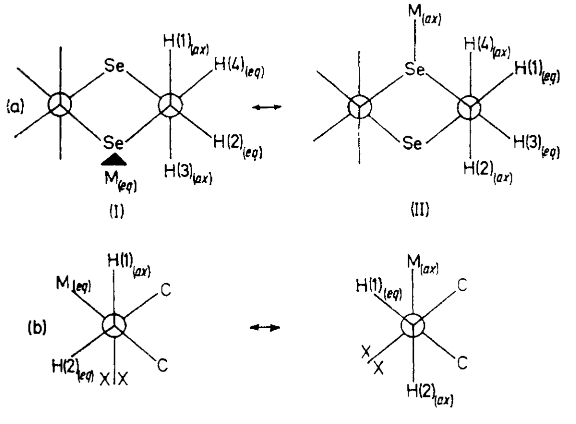

FIGURE 2 1,4-Diselenan co-ordinated as a monodentate ligand: (a) viewed along a C–C; (b) viewed along a C–Se bond

$$\nu_{\mathrm{H(1)}} = P_{\mathrm{I}}\nu_{\mathrm{H(1)}(ax)} + P_{\mathrm{II}}\nu_{\mathrm{H(1)}(eq)} \quad (1)$$

$$\nu_{\mathrm{H(2)}} = P_{\mathrm{I}}\nu_{\mathrm{H(2)}(eq)} + P_{\mathrm{II}}\nu_{\mathrm{H(2)}(ax)} \quad (2)$$

$$\nu_{\mathrm{H(3)}} = P_{\mathrm{I}}\nu_{\mathrm{H(3)}(ax)} + P_{\mathrm{II}}\nu_{\mathrm{H(3)}(eq)} \quad (3)$$

$$\nu_{\mathrm{H(4)}} = P_{\mathrm{I}}\nu_{\mathrm{H(4)}(eq)} + P_{\mathrm{II}}\nu_{\mathrm{H(4)}(ax)} \quad (4)$$

$$J_{1,3} = P_{\mathrm{I}}J_{1(ax),3(ax)} + P_{\mathrm{II}}J_{1(eq),3(eq)} \quad (5)$$

$$J_{2,4} = P_{\mathrm{I}}J_{2(eq),4(eq)} + P_{\mathrm{II}}J_{2(ax),4(ax)} \quad (6)$$

$$J_{1,4} = P_{\mathrm{I}}J_{1(ax),4(eq)} + P_{\mathrm{II}}J_{1(eq),4(ax)} \quad (7)$$

$$J_{2,3} = P_{\mathrm{I}}J_{2(eq),3(ax)} + P_{\mathrm{II}}J_{2(ax),3(eq)} \quad (8)$$

observed even when $P_{\mathrm{I}} = P_{\mathrm{II}}$, as $\nu_{\mathrm{H(1)}(ax)} \neq \nu_{\mathrm{H(2)}(ax)}$ and $\nu_{\mathrm{H(1)}(eq)} \neq \nu_{\mathrm{H(2)}(eq)}$. However, these differences would probably be very small and the expected spectrum would be an AA'BB' multiplet, but with only two sets of vicinal coupling constants, $J_{1,3} = J_{2,4}$ and $J_{1,4} = J_{2,3}$. Moreover, the relative conformer populations would be temperature dependent and the observance of temperature-invariant AA'BB' spectra, each with three different vicinal coupling constants, conclusively shows that 1,4-diselenan does not co-ordinate as a monomeric ligand in these complexes.

Chelated 1,4-diselenan requires the ligand to exist in a boat conformation. With the increase in the size of the metal atom from chromium to tungsten, it might be expected that the ligand would co-ordinate in a flexible twist-boat conformation in order to vary readily the distance between the two ligand atoms. However, such a conformation would give an unsymmetrical ABCD spectrum and can thus be discounted. A regular, selenium–selenium prow, boat conformation requires that the methylene protons of the ligand are eclipsed. It is well established that eclipsed methylene groups are *ca.* 12 kJ mol^{-1} less favourable than staggered methylene groups and a boat conformation for a free six-membered ring is invariably less energetically favourable than a chair conformation. Consequently, isolation of a boat conformation for any six-membered ring is a rare occurrence, although this has been achieved in molecules such as 1,4-diazabicyclo[2.2.2]octane in which the six-membered rings are held in the boat conformation by bridging groups.[16]

The complexes can be alternatively viewed as two fused five-membered chelate ring systems, the molecule as a whole having C_{2v} symmetry. An analogy can be drawn between these complexes and norbornane (Figure 3), the bridgehead carbon atom being replaced by a metal atom in the complexes, and there is encouraging agreement between the n.m.r. spectral parameters found for the two types of compound. The origin of the chemical shift differences between *endo*- and *exo*-protons, $\Delta_{\nu\mathrm{AB}} =$ 0·34—0·69 p.p.m. for the complexes and $\Delta_{\nu endo\text{-}exo}$ *ca.* 0·50 p.p.m. for norbornane derivatives,[17] is probably the same in both groups of compounds and possibly arises from molecular anisotropy effects. There can be little doubt about the assignment of the negative coupling constants J_{AB} and $J_{\mathrm{A'B'}}$ to the geminal coupling constants as their values are typical of those found for sp^3 hybridised methylene groups.[18]

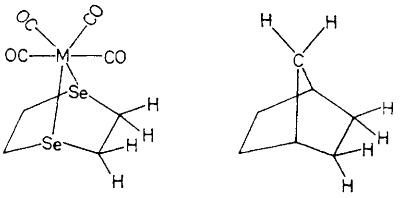

FIGURE 3 Postulated structure for LM(CO)$_4$ compared with norbornane

Norbornanes, being rigid molecules with fixed, often accurately known, dihedral angles, have proved particularly interesting for study as conformational standards.[19] The relationship between vicinal proton couplings and the H–C–C–H dihedral angles is given by a Karplus equation of the type (9) where ϕ is the dihedral

$$J = A\cos^2\phi + n\cos\phi \quad (9)$$

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[16] D. B. McDonald, Ph.D. Thesis, University of Liverpool, 1966, quoted by W. A. Thomas, *Ann. Rep. N.M.R. Spectroscopy*, 1968, **1**, 72.

[17] J. I. Musher, *Mol. Phys.*, 1963, **6**, 93.

[18] Ref. 10, p. 129.

[19] See, *e.g.* F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Amer. Chem. Soc.*, 1967, **89**, 4431.

angle and A and n are constants whose actual values are sensitive to certain factors including the chemical environments of the protons.[20] For norbornane-type molecules, $J_{endo\text{-}endo}$ and $J_{exo\text{-}exo}$, where $\phi = 0$, are as expected larger than $J_{endo\text{-}exo}$ and $J_{exo\text{-}endo}$, where $\phi = ca.\ 120°$. Moreover, although the dihedral angles are the same in both cases, $J_{endo\text{-}endo}$ is invariably smaller than $J_{exo\text{-}exo}$. This inequality, which has not yet been adequately explained, apparently varies according to the compound and can be quite substantial.[17,19] A similar pattern of vicinal coupling constants is apparent for the complexes. The largest coupling constants are $J_{AA'}$ and $J_{BB'}$ and by analogy with norbornanes can probably be respectively assigned to $J_{exo\text{-}exo}$ and $J_{endo\text{-}endo}$. The remaining, smaller coupling constants, $J_{AB'}$ and $J_{A'B}$ are equal in magnitude and are assigned to $J_{endo\text{-}exo}$ and $J_{exo\text{-}endo}$.

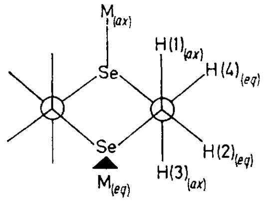

FIGURE 4 1,4-Diselenan in the chair conformation and bridging the metal atoms

Finally, for completeness, it is of interest to consider the form of the n.m.r. spectrum which would be expected for a dinuclear species with two bridging ligands in the chair conformation such as proposed by Hendra.[13] Such bridging can only be accomplished when one ligand atom co-ordinates *via* an equatorial lone pair, while the other co-ordinates *via* an axial lone pair. This situation is illustrated by Figure 4. Therefore, each ligand in a chair conformation cannot be centrosymmetric, although the molecule as a whole would possess a centre of symmetry. Conformational mobility would be very restricted in such a molecule and both ligands would have the same n.m.r. spectrum. This would consist of an unsymmetrical ABCD multiplet, although in the event that $\nu_{H(1)(ax)} \simeq \nu_{H(3)(ax)}$ and $\nu_{H(2)(eq)} \simeq \nu_{H(4)(eq)}$, it would approximate to an $AA'BB'$ multiplet. For this $AA'BB'$ multiplet, the order of magnitude of the vicinal coupling constants would be $J_{1,3} > J_{2,3} = J_{1,4} > J_{2,4}$ as $J_{ax\text{-}eq}$ is almost invariably greater than $J_{eq\text{-}eq}$.[16]

Thus it can be seen that, provided the spectra are examined over a wide temperature range and are sufficiently well resolved to be analysable, n.m.r. spectroscopy provides a powerful method for deciding the structures of soluble complexes of 1,4-disubstituted cyclohexane type ligands.

EXPERIMENTAL

1,4-*Diselenan*.—This compound was prepared by published procedures.[21]

Interaction of 1,4-*Diselenan with Bicyclo*[2.2.1]*heptadienetetracarbonylmetal*.—The requisite carbonyl complex (*ca.* 0·5 g) was refluxed under nitrogen for 30 min in n-heptane with the stoicheiometric amount of 1,4-diselenan. The hot solution was filtered and on cooling the filtrate, yellow-green crystals of 1,4-*diselenantetracarbonylmetal* were obtained: *chromium complex* (Found: C, 26·0; H, 2·4. $C_8H_8O_4CrSe_2$ requires C, 25·4; H, 2·1%); *molybdenum complex* (Found: C, 23·5; H, 2·3. $C_8H_8O_4MoSe_2$ requires C, 22·8; H, 1·9%); *tungsten complex* (Found: C, 19·4; H, 1·8. $C_8H_8O_4WSe_2$ requires C, 18·9; H, 1·6%).

N.m.r. Spectra.—These were obtained using a Bruker 90 MHz n.m.r. spectrometer.

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[20] M. Barfield and D. M. Grant, *Adv. Magnetic Resonance*, 1965, **1**, 144.

[21] J. D. McCullough and N. Tideswell, *J. Amer. Chem. Soc.*, 1954, **76**, 3091.