Structure and Bonding in some Simple Tungsten Compounds. Deductions from Tungsten-182 Mössbauer Spectra

By **Alfred G. Maddock, Roger H. Platt, and Alan F. Williams,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Ramon Gancedo, Instituto de Quimica Fisica ' Rocasolano ', Serrano 119, Madrid 6, Spain

The Mössbauer spectra of several simple tungsten compounds have been measured, using the 100 keV transition of tungsten-182. The Mössbauer quadrupole coupling is extremely sensitive to an asymmetric environment, and this enables much information on the electron distribution in tungsten compounds to be obtained. The results are considered in relation to the structure and bonding of the compounds studied; the large quadrupole couplings observed with many compounds are explained in terms of covalent bonding, with considerable variation in the bond order.

We have previously reported the results of preliminary investigations into the chemical applications of Mössbauer spectroscopy using the 100 keV transition of tungsten-182,[1] and here we give results for a variety of simple inorganic tungsten compounds.

The 100 keV transition of tungsten is between the excited, $I = 2$, state and the ground state, $I = 0$, the excited state being conveniently fed by the decay of ^{182}Ta (half-life 115 days), although many other γ-rays are emitted in the complex decay scheme. The value of $\delta R/R$ for this transition is extremely small, and although isomer shift values have been reported,[2] we have not observed shifts greater than the experimental errors. The quadrupole moment of the excited state is however large[3] (1·80 barns), and negative,[4] and this enables quadrupole coupling constants to be measured with reasonable accuracy. The Heisenberg linewidth of the transition is 2 mm s^{-1}, and the linewidths observed are not appreciably greater,[5] while quadrupole interactions of several times this magnitude are frequently observed. In the absence of a magnetic field, the $I = 2$ level is split into five levels given by equations (1a—e).

$$E = \frac{e^2Qq}{24}\begin{cases} 6\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}} & & (1a) \\ & |M_{\text{I}}| = 2 & \\ 6 & & (1b) \\ -3(1-\eta) & & (1c) \\ & |M_{\text{I}}| = 1 & \\ -3(1+\eta) & & (1d) \\ -6\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}} & M_{\text{I}} = 0 & (1e) \end{cases}$$

The pure quadrupole ($E2$) transition results in all 5 lines in the Mössbauer spectrum having equal intensity, and in the presence of a non-zero asymmetry parameter η the removal of the degeneracy of levels (1c) and (1d) is sufficiently great for η values to be determined. The asymmetry of the energy levels enables the sign of the quadrupole coupling and hence of the electric field gradient to be determined.

EXPERIMENTAL

Source of Compounds.—Commercial samples of $(NH_4)_2WS_4$ (98%), W_2C (99·8%), W_2N (90%) supplied by ROC/RIC at the purities quoted in parentheses, and $SiO_2.12WO_3.$-$26H_2O$ from BDH were used. Me_2SnWO_4,[6] $K_3W_2Cl_9$,[7] Et_4NWCl_6,[8] and $WOCl_4$[9] were prepared as described in the literature. $Na_2W_2O_7$ and $Li_2W_2O_7$ were prepared by fusion at 800 °C of stoicheiometric amounts of WO_3 and alkali-metal carbonate. WS_3 was prepared by heating $(NH_4)_2WS_4$ as described in ref. 10. The samples of tungsten bronzes were kindly given by Dr. P. Dickens.

Mössbauer Measurements.—All spectra (with the exception of some of the bronzes) were taken at liquid helium temperature using a conventional constant acceleration spectrometer. The source was ^{182}Ta in Ta metal and the 100 keV γ-rays were detected with a Ge(Li) detector, enabling complete resolution from other radiation.

The high energy of the Mössbauer transition results in rather low recoil free fractions giving a typical absorption of 1%; it is thus desirable to use fairly thick absorbers, but unfortunately, with increasing thickness of absorber the accuracy of the determination of hyperfine parameters from the computer fitting of Lorentzian lines decreases considerably.[11] The thickness effect is determined by the ' peak absorbance ' defined by Stone[12] as $n\sigma f\Gamma/\Gamma_0$ where n = number of Mössbauer nuclei cm^{-2}, σ = absorption cross section of the Mössbauer nucleus, f = the recoil free fraction, and Γ,Γ_0 = the observed and Heisenberg line widths; for a single line absorber with $f = 0{\cdot}15$, a thickness of 25 mg cm^{-2} of tungsten metal corresponds to a peak absorbance of 1. For a quadrupole split absorber the effective value of n is smaller (reduced by 80% if all five lines are resolved) and thus quadrupole split spectra are less sensitive to thickness effects. We generally used a thickness of 60 mg cm^{-2} of tungsten metal; this thickness will not appreciably perturb the spectra for $ce^2qQ/E_\gamma \geqslant 4$ mm s^{-1}. Where this thickness would not give reasonable absorption, it was attributed to a low f value and a thicker sample was tried; the low f value reduces the perturbation due to thickness effects.

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[9] H. Hess and H. Hartung, *Z. anorg. Chem.*, 1966, **344**, 157.

[10] J. C. Wildervanck and F. Jellinek, *Z. anorg. Chem.*, 1964, **328**, 309.

[11] See. for example, E. Gerdan, W. Rath, and H. Winkler, *Z. Phys.*, 1972, **257**, 29.

[12] A. J. Stone, *Nuclear Inst. and Meth.*, 1973, **107**, 285.

The computer fitting of the recorded spectra was accomplished using the procedure described by Stone [13] where the function fitted is the sum of five Lorentzian lines of equal width and intensity whose relative positions are given by equations (1a—e). In most cases η was constrained to be zero since an unconstrained fit generally diverged giving little improvement in χ^2. A small variation in η may allow the program to fit more satisfactorily spectra where there are saturation effects or a large amount of statistical noise, without having in itself any physical meaning, and without giving more than a minimal improvement in the χ^2 value; we have regarded η values of less than 0·2 as zero. We feel that the good χ^2 values obtained using a fit dependent on only 4 parameters (position, line width, total intensity, and quadrupole splitting) are sufficient justification for this method. In cases where e^2qQ is less than 4 mm s^{-1} the fitting program was not able to distinguish the sign of the splitting, and we have therefore reported such spectra as broadened single lines.

RESULTS

The results are summarised in the Table.

In this section we correlate the quadrupole coupling data with the molecular structure of the compounds investigated.

Compound	Width mm s^{-1}	e^2Qq mm s^{-1}	η	ψ^2/d.f.
WS_3	3·43	−7·72	0	392/392
W_2N	3·39	±2·25	0	428/392
W_2C	3·20	+7·38	0	356/391
WO_3 (ref. 1)	2·50	−8·30	0·62	480/389
$SiO_2,12WO_3,26H_2O$	3·60	−18·13	0·42	281/191
$Na_2W_2O_7$ (2 sites)	2·31	+10·29	0·95	409/386
	2·24	−3·42	0·95	
$Li_2W_2O_7$ (2 sites)	2·78 [a]	−11·66	0·83	409/388
	2·78 [a]	+5·95	0·71	
$Ba_3Fe_2SO_9$	3·30	±3·15	0	407/391
$WOCl_4$	3·52	0	0	
Me_2SnWO_4	2·81	−9·32	0·71	396/391
$(NH_4)_2WS_4$	2·88	−8·31	0·76	363/390
$K_3W_2Cl_9$	2·24	+8·89	0	385/391
Et_4NWCl_6	3·95	−12·58	0	174·5/190
Et_4NWCl_6	4·0	−12·3	0·4	174/189

or, for Et_4NWCl_6, five lines of equal width and intensity, width 3·3 mm s^{-1}, positions: 3·7, 1·8, 0·7, −2·9, −3·9 mm s^{-1}, ψ^2 = 171/187.

Tungsten bronzes

Compound	Thickness mg cm^{-2}	Width mm s^{-1}	Intensity [b]	ψ^2/d.f.
$Na_{0·53}WO_3$	35	1·91	0·014	183/191
$Na_{0·53}WO_3$	70	3·04	0·163	219/191
$Na_{0·53}WO_3$	140	4·28	0·220	201/191
$Li_{0·36}WO_3$	180	5·25	0·128	390/391
80 K	180	4·34	0·021	362/391

Error ±0·2 mm s^{-1}.

[a] Constrained to be equal. [b] Normalised to unit baseline, in mm s^{-1}. All spectra taken at 4·2 K unless otherwise stated. Where a parameter is given as zero it was constrained to be so during the fitting. For the bronzes, quadrupole splittings and magnetic splittings were constrained to be zero.

WS_3, W_2N, *and* W_2C.—These compounds have close packed structures whose physical properties suggest well developed band structures, and they give fairly high recoil free fractions. It is of interest that WS_3 gives a quadrupole coupling of the opposite sign to WS_2 and of the same sign as WO_3 although with a zero asymmetry parameter; unfortunately the amorphous nature of this compound has precluded *X*-ray structure determination.[10] The single line spectrum of W_2N is to be expected from its cubic close packed structure; [14] the broad line observed is probably a thickness effect, although it might be due to impurities or non-stoicheiometry. W_2C gives a quadrupole coupling as a result of its hexagonal environment,[15] rather close to the value obtained for the tungsten dichalcogenides on whose spectra we comment in another paper.[16] The co-ordination in the chalcogenides is also of hexagonal symmetry (trigonal prismatic), and it is unfortunate that isomer shift results are not available to provide further information about the nature of the electron distribution in this type of compound.

Oxide Systems: WO_3, $SiO_2.12WO_3.26H_2O$, $Na_2W_2O_7$, $Li_2W_2O_7$, *and* $Ba_3Fe_2WO_9$.—The oxide systems formed by tungsten are amenable to study by Mössbauer spectroscopy since they also give fairly high recoil free fractions, and quadrupole coupling constants vary considerably.

The most symmetric environment encountered is in $Ba_3Fe_2WO_9$ where the immediate co-ordination of the tungsten atom is by six octahedrally disposed oxygen atoms and the lowering of the site symmetry to C_{3v} is due to the nearest cations, the structure being the hexagonal $BaTiO_3$ perovskite structure.[17] This compound gives a broadened single line spectrum; the broadening may be due to a saturation effect, and no determination of the sign of the quadrupole coupling was possible.

In all the other compounds the co-ordination of the oxygen atoms to the tungsten atom is irregular, and large quadrupole couplings were observed. WO_3, whose structure is distorted ReO_3 type,[18] gives a considerable quadrupole splitting and an intermediate asymmetry parameter; an even more irregular environment is indicated in SiO_2.-$12WO_3.26H_2O$. The structure of the isomorphous phosphate analogue of this compound has been determined,[19] and the tungsten atoms are found in 4 groups of 3 WO_6 octahedra surrounding a PO_4 tetrahedron. The W–O distances vary considerably with 3 at 1·85 Å, 2 at 2·0 Å, and 1 at 2·34 Å, and the oxygen oxygen distances are all different. The very large quadrupole coupling shown by this compound [greater even than that for a compound with 2 non-bonding 5*d* electrons, $K_4W(CN)_82H_2O$], indeed the greatest yet recorded, is extremely interesting; the broad lines obtained may be a result of slight differences between the 3 tungsten sites. Although the tungsten is formally in a +6 (d^0) oxidation state, the bonding must be very covalent, and it seems reasonable to suppose that the electric field gradient arises from the different orders of the bonds to the oxygen atoms at different distances. A similar sensitivity to bond length is encountered in $Na_2W_2O_7$ whose structure has been determined as chains of WO_6 octahedra sharing two opposite apices, with WO_4 tetrahedra bridging two octahedra and sharing an oxygen with each.[20] The larger quadrupole split component is presumably due to the tetrahedral site where the W–O distances vary considerably (2 oxygens at 1·78 Å, 2 at 1·93 Å), while the smaller quadrupole coupling of the octahedral site reflects the smaller distortions. Both sites have an η value close to 1, to be

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[13] A. J. Stone, Appendix to *J. Chem. Soc.* (*A*), 1967, 1966.

[14] A. F. Wells, 'Structural Inorganic Chemistry,' 3rd edn., Oxford, p. 1020.

[15] Ref. 14, p. 1018.

[16] M. G. Clark, R. Gancedo, A. G. Maddock, A. F. Williams, and A. D. Yoffe, *J. Phys.* (*C*), 1973, **6**, 474.

[17] G. Blasse, *J. Inorg. Nuclear Chem.*, 1973, **35**, 680.

[18] Ref. 14, p. 469.

[19] J. F. Keggin, *Proc. Roy. Soc.*, 1934, **144**, 75.

[20] I. Lindquist, *Acta Chem. Scand.*, 1950, **4**, 1066.

expected for the tetrahedral site which is an A_2B_2W system.[21] The spectrum of $Li_2W_2O_7$ is considerably less well resolved, but it is sufficiently different to suggest that it is not isostructural with $Na_2W_2O_7$.

$WOCl_4$.—The single line spectrum of this compound is surprising since the tungsten environment in this compound is markedly asymmetric. The structure consists of WO_2Cl_4 octahedra linked by shared opposite oxygen atoms; the W–O distances are not however equal (1·8 Å and 2·2 Å) and the Cl_4 plane is in between the tungsten atom and the more distant oxygen atom.[10] The spectrum is a single line, although the width is rather large. We can only suggest that the distortion of the Cl_4 plane below the tungsten atom compensates for the e.f.g. due to the different W–O distances, but this explanation is not satisfying; in view of the extreme sensitivity to an irregular environment shown by the Mössbauer spectra in, for example, the oxides, a coincidental cancellation of e.f.g. contributions seems unlikely.

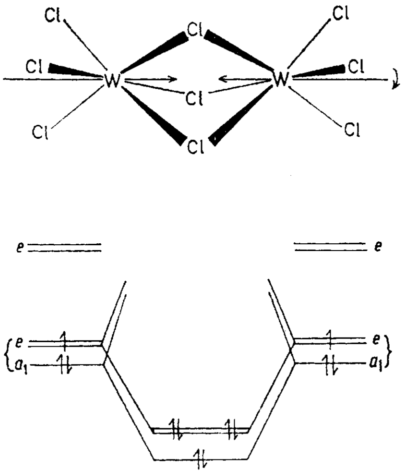
Me_2SnWO_4.—Me_2SnWO_4 is a compound of interest in that it contains two Mössbauer nuclei. The Mössbauer parameters of the tin atom have been measured, and are reported as $\delta(SnO_2)$ 1·29 ± 0·05, $\Delta = 3{\cdot}53 \pm 0{\cdot}05$ mm s^{-1}.[22] In a paper on a series of di- and tri-alkyl tin derivatives, including Me_2SnSO_4 and Me_2SnSeO_4, Ford, Sams, Goel, and Ridley reported similar results for tin Mössbauer parameters (although δ and Δ were both slightly greater), and postulated the presence of *trans* octahedral Me_2SnO_4 groups and tetrahedral XO_4 groups.[23] The tin Mössbauer parameters Me_2SnWO_4 are certainly similar to those for Me_2Sn(acetylacetone)$_2$ ($\delta = 1{\cdot}18$ mm s^{-1}, $\Delta = 3{\cdot}93$ mm s^{-1}).[24]

The tungsten Mössbauer spectrum does however suggest that the WO_4 tetrahedron must be significantly distorted to give so large a quadrupole coupling and asymmetry parameter. The value of e^2Qqc/E_γ is close to that for the tetrahedral site in $Na_2W_2O_7$, and since the asymmetry parameters are near 1 the difference in sign is of little significance. The asymmetry may be explained on the basis of the model of Ford *et al.* by assuming that two of the WO_4 oxygen atoms interact more strongly with the tin atom than the other two; this would lead to a slight inequivalence of the oxygens co-ordinating the tin, but the quadrupole splitting might not be sensitive enough to show this. There cannot be said to be any confirmation of the structure of this compound from the Mössbauer spectrum, but it is at least consistent with a structure of WO_4 tetrahedra sharing (in a non-symmetric fashion) all its oxygen atoms with linear Me_2Sn groups to give a polymeric structure in which the tin has a co-ordination number of six (co-ordinated to two methyl and four WO_4 groups).

The Tungsten Bronzes.—All the tungsten bronzes investigated were in the cubic, metallic composition phase,[25] and gave single line spectra showing saturation effects. Some absorption at liquid nitrogen temperature was obtained, but the saturation effects due to the thick sample needed were so great as to vitiate the results. It would be interesting to study the spectrum as the amount of alkali metal present was reduced, and to observe the effects on the spectrum of the metal–non-metal transition, and the transition from cubic (perovskite type) structure to lower symmetry. The results at present only serve to confirm the equivalence of all the tungsten atoms in the metallic phase.

$(NH_4)_2WS_4$.—This compound has a structure consisting of WS_4^{2-} tetrahedra linked through NH_4^+ ions in $-NH_4-S-NH_4-S$ chains parallel to the z axis with two sulphur atoms from each tetrahedron involved in the linkage; the environment of the tungsten atom is thus the tetrahedral A_2B_2W type and an asymmetry parameter of near 1 would be expected; a value of 0·76 is observed. The X-ray structure determination[26] shows the WS_4^{2-} tetrahedron to be virtually undistorted and the W–S bond lengths identical to within 0·01 Å, which is surprising in view of the interactions with the NH_4^+ groups shown by two of the four sulphur atoms. The considerable quadrupole coupling of $-8{\cdot}3$ mm s^{-1} observed is indicative of considerable electronic asymmetry.

Perhaps the most plausible explanation is of stronger π-interactions with the lone sulphur atoms, although it is surprising that this gives no noticeable change in bond length. The quadrupole coupling must be caused by asymmetry of bonding since it is an order of magnitude too great to be caused by the isolated NH_4^+ ions. It is worth noting that the X-ray result would not predict so large an asymmetry, and suggests that deductions of electron distribution from X-ray diffraction data (that is, bond lengths) should be made with care.



$K_3W_2Cl_9$.—The only d^3 complex we have studied, the $W_2Cl_9^{3-}$ ion has the structure of two WCl_6 octahedra sharing a face to give D_{3d} symmetry with the threefold axis passing through the two tungsten nuclei.[27] This would indicate the observed asymmetry parameter of zero, but the small magnitude of the quadrupole coupling is rather surprising, since the W–W distance is reduced to 2·409 Å, less than in tungsten metal (2·519 Å), and close to the value suggested for a W–W double bond. A considerable amount of metal–metal bonding must be involved and this must be the cause of the diamagnetism of this compound.[28]

A drawing of the structure, and the ligand field energy level diagram for this ion are given in the Figure. Since $d_{x^2-y^2}, d_{xy}$, and d_{xz}, d_{yz} all have e_g symmetry, the second level

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[21] M. G. Clark, *Mol. Phys.*, 1972, **20**, 257; *Chem. Phys. Letters*, 1970, **6**, 558.

[22] M. Vucelic, *Croat. Chem. Acta*, 1968, **40**, 225.

[23] B. F. E. Ford, J. R. Sams, R. G. Goel, and D. R. Ridley, *J. Chem. Soc.* (*D*), 1969, 71.

[24] B. W. Fitzsimmons, N. J. Seeley, A. W. Smith, *J. Chem. Soc.* (*A*), 1969, 143.

[25] P. G. Dickens and M. S. Whittington, *Quart. Rev. Chem. Soc.*, 1968, **22**, 30.

[26] K. Sasvari, *Acta Cryst.*, 1963, **16**, 719.

[27] W. H. Watson and J. Waser, *Acta Cryst.*, 1958, **11**, 689.

[28] P. D. W. Boyd, P. W. Smith, and A. G. Wedd, *Austral. J. Chem.*, 1969, **22**, 653.

will be a mixture of these levels. If we assume the lower e_g level to be almost completely non-bonding to the chlorine ligands, then this e_g level and the $a_{1g}(d_{z^2})$ level are free to interact with their sibling orbitals on the neighbouring tungsten atom. A simple molecular orbital diagram for the interaction may be drawn, and a bonding configuration derived; from this model we may obtain a value for the quadrupole coupling.

As $d_{x^2-y^2}$ gives the same contribution to the electric field gradient as d_{xy}, and d_{xz} the same as d_{yz}, in calculating the e.f.g. it is possible to represent the e orbitals for one of the tungsten atoms by

$$\begin{array}{rcccl} |e_\kappa\rangle & = & \cos\alpha|d_{2\kappa}\rangle & + & \sin\alpha|d_{1\kappa}\rangle \\ & & (x^2-y^2, xy) & & (xz, yz) \text{ components} \end{array}$$

where $\kappa = c$ or s are the two orthonormal components of the $d_{x^2-y^2}$, d_{xy}, or $d_{xz,yz}$ subshells. The lowest energy orbital is the $A_1(d_{z^2})$. If the high energy e_g orbitals and the 6s and 6p are assumed to be involved in equivalent W–Cl σ bonds of approximately octahedral symmetry, then the e.f.g. is determined only by the two lowest levels. We may now calculate the e.f.g. very roughly by taking the following simple molecular orbitals:

$$|a_{1g}\rangle = \frac{1}{\sqrt{2}}\left(|d_{z^2}^{(1)}\rangle + |d_{z^2}^{(2)}\rangle\right)$$

$$|e_g\rangle = \frac{1}{\sqrt{2}}\left(|e_\kappa^{(1)}\rangle + |e_\kappa^{(2)}\rangle\right) \qquad \kappa = s,c$$

where the superscripts denote the different tungsten atoms.

Using the e.f.g. operator V_{zz} and ignoring contributions from atom 2 at nucleus 1 and any overlap terms gives the e.f.g. as:

$$q = \tfrac{1}{2}\langle d_{z^2}^{(1)}|V_{zz}|d_{z^2}^{(1)}\rangle + \tfrac{1}{2}\sum_{\kappa}\langle e_\kappa^{(1)}|V_{zz}|e_\kappa^{(1)}\rangle \qquad \kappa = s,c$$

at atom 1. We may substitute for e, and also for $\langle d_{z^2}^{(1)}|V_{zz}|d_{z^2}^{(1)}\rangle$ since this term is no more than the electronic component of the quadrupole coupling due to one d-electron that we have derived from the octacyanides to be 16 mm s^{-1}.[29] A comparison with the observed value of +8·9 mm s^{-1} may now be made:

$$e^2Qqc/E_\gamma = 16 - 32\cos^2\alpha + 16\sin^2\alpha = 8{\cdot}9 \text{ mm s}^{-1}$$

Solving for $\cos^2\alpha$ gives a value of *ca.* 0·5, implying that the e orbitals are equal mixtures of $d_{xy}, d_{x^2-y^2}$, and $d_{xz,yz}$; this enables the tungsten metal–metal bond to be formulated as one σ, one π, and one δ bond, although the accuracy of the calculation is such that it is perhaps better to consider the multiple bond as a mixture exhibiting both π and δ character.

However naïve the above explanation is, the qualitative deductions are clear: the diamagnetism must be due to bonding since an exchange interaction would give a magnetic field at the tungsten nucleus, and no magnetic splitting is observed. The large electric field gradient expected from a single bond is not observed, and this must be reduced by occupation of higher order bonding orbitals. While the distortion of the WCl_6 octahedron on squashing has not been allowed for, the effect of this should be less than that of the 'non-bonding' d electrons, and it is reasonable to invoke a high degree of multiple bonding in the $W_2Cl_9^{3-}$ anion.

Et_4NWCl_6.—This compound gave a Mössbauer spectrum showing a typical quadrupole split pattern, and a computer fit with $\eta = 0$ gave a good χ^2 value with $e^2qQc/E_\gamma = -12{\cdot}6$ mm s^{-1}. Assuming the WCl_6^- unit to be approximately octahedral, this large negative value corresponds to a large distortion from ideal geometry. A large distortion was also postulated in Et_4NMoCl_6 [30] from its e.s.r. spectrum; the value of the quadrupole coupling is almost as large as that assigned to one d-electron (16 mm s^{-1}), the reduction presumably coming from asymmetry in the σ-bonding as a result of the distortion.

In a study of the magnetic properties of this compound [8] it was claimed that Et_4NWCl_6 was antiferromagnetic with a Neel temperature of 140 K, although unfortunately only a few measurements below this temperature were made. The magnetic susceptibility is very low: at room temperature $\chi_M = 168{\cdot}4 \times 10^{-6}$ c.g.s. units; this value was very nearly constant until 140 K when it began to fall to $87{\cdot}8 \times 10^{-6}$ c.g.s. units at 82 K, the lowest temperature reached. In the discussion the effects of spin–orbit coupling and distortion were not considered; the crystal structure of this compound has not been determined.

Further uncertainty as to the antiferromagnetic nature of this compound comes from the Mössbauer spectrum: little evidence of magnetic interaction is shown in the spectrum; the maximum value of the internal field which would not unduly affect the spectrum is 20 tesla; in K_2IrCl_6 (low-spin d^5) a Mössbauer study revealed an internal field of 40 T and a Neel temperature of the order of 4 K, indicating much weaker exchange interactions.[31] The differences between WCl_6^- and $IrCl_6^{2-}$ may be pursued further by noting the very small quadrupole coupling constant measured for $IrCl_6^{2-}$, indicating virtually no distortion. In view of the similarities to be expected between a d^1 and d^5 low-spin system, the picture of Et_4NWCl_6 as an antiferromagnetic species with regular WCl_6^- octahedra appears inadequate; regrettably, our spectrum is not of sufficiently high quality to allow complete rejection of an internal field, but any field present must be very small, probably less than 10 T, and certainly less than 20 T. A summary of the various fits made to this spectrum is given in the Table; the variation in line position and width on removing constraints is probably a result of the poor quality of the spectrum since the improvement in χ^2 is minimal.

Electronic and vibrational spectroscopic studies of this compound have been made: the electronic absorption spectrum is not inconsistent with a spread of up to 5000 cm^{-1} in the t_{2g} levels,[32] and the W–Cl frequency in the i.r. spectrum showed some evidence of splitting, although this was attributed to instrumental aberrations.

DISCUSSION

We now summarise our conclusions concerning the electronic structure of tungsten compounds and attempt some comparison with results obtained with other Mössbauer isotopes. The compounds we have studied have been relatively simple, and have been restricted by the low recoil free fractions to fairly strongly bound systems, nevertheless large quadrupole couplings have

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[29] M. G. Clark, R. Gancedo, A. G. Maddock, and A. F. Williams, unpublished results.

[30] J. F. Gibson and R. Dowsing, *J. Chem. Soc.* (*A*), 1967, 655.

[31] F. E. Wagner and U. Zahn, *Z. Phys.*, 1970, **233**, 1.

[32] B. J. Brisden and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1101; B. J. Brisden, R. A. Walton, and P. C. Crouch, *Spectrochim. Acta*, 1968, **24A**, 601; B. J. Brisden, R. A. Walton, D. A. Edwards, D. J. Machin, and K. S. Murray, *J. Chem. Soc.* (*A*), 1967, 1825.

been observed and only in $Ba_3Fe_2WO_9$, which possesses a closed packed perovskite structure, W_2N with a cubic structure, and the bronzes were no quadrupole interactions seen. The most striking observation is the large quadrupole couplings in the W^{VI} oxide systems with a formal d^0 configuration; from ^{57}Fe Mössbauer studies one would expect only a lattice term (of a small magnitude) in the quadrupole coupling, while in tungsten the largest quadrupole coupling we have yet recorded is found in $12WO_3SiO_2,26H_2O$, a d^0 species. In compounds where there are formally non-bonding *d* orbitals occupied, such as Et_4NWCl_6 and the octacyanide species $W(CN)_8{}^{4-}$ and $W(CN)_8{}^{3-}$ on which we report elsewhere,[29] the quadrupole splittings are substantially smaller than a calculation of their magnitude from consideration of $\langle r^{-3}\rangle_{5d}$ values.

The obvious reasons for the failure of established methods of interpretation of quadrupole coupling in terms of ions are the extremely covalent nature of tungsten chemistry, and the change in electronic structure due to distortion from regular geometry. The picture of the Mössbauer nucleus which is so successful for simple iron compounds, of a spherical atom whose *d* orbitals interact feebly with the ligands, their degeneracy being lifted but not being appreciably mixed, is not applicable, and it is necessary to resort to a molecular orbital theory.

This is also problematic; the application of a simple theory such as that used for tin(IV) compounds[33] is impossible since several of the assumptions of the model are no longer valid. The model was intended for compounds where the tin atom is bonded covalently to a small number of ligands; for tungsten compounds with high co-ordination numbers and irregular bond lengths, this is unrealistic, and the other assumption of constant character of a given metal–ligand bond and of small ligand–ligand interactions are clearly invalid. In compounds where there are well developed band structures, as in many binary compounds, hybridisation of bands makes definition of the occupied orbitals difficult, and hence accurate calculations of the quadrupole coupling are not possible.

It is not even clear which orbitals are most important in determining the electric field gradient. The 5*d*, 6*s*, and 6*p* orbitals will all be populated to some extent, and the contribution of the 6*p* to the e.f.g. is difficult to estimate; a simple Hermann–Skillmann[34] calculation suggests that when the population of the 5*d* orbitals is low, $\langle r^{-3}\rangle_{6p}$ is almost as large as $\langle r^{-3}\rangle_{5d}$. However questionable the use of the Hermann–Skillman program for this sort of calculation, the 6*p* orbitals must have an appreciable effect. The simplification possible in the simple models for iron and tin, that the quadrupole coupling is determined by imbalance in the population of only one atomic subshell (3*d* in iron, 5*p* in tin), may not be permissible for tungsten. Only where the symmetry of the tungsten nucleus is high (as in $K_3W_2Cl_9$) has it been possible to reach any qualitative conclusions from orbital arguments.

It is pertinent to consider whether the electronic asymmetry arises from asymmetric σ or π bonding. In the case of a tetrahedrally co-ordinated entity such as $WS_4{}^{2-}$ some π interaction is necessary to satisfy the electroneutrality principle, and, in view of the high symmetry of the co-ordination sphere in $(NH_4)_2WS_4$, asymmetric π bonding is the only way to explain the quadrupole coupling. In octahedrally co-ordinated tungsten compounds, asymmetric σ bonding alone is sufficient to explain the results, but in a nuclear quadrupole resonance study of K_2WCl_6 the π bond order of each W–Cl bond was estimated as 0·2.[35] It might be claimed that the quadrupole coupling arises from π interactions with the unshared oxygen atoms in the oxides, but such an explanation would not cover, for example, the considerable quadrupole coupling in WO_3 where all the oxygens are shared. A distribution between π and σ bonding is not possible from Mössbauer measurements alone, but, in compounds where co-ordination polyhedra are linked together there is likely to be considerable electron delocalisation, and the distinction is rather meaningless.

In conclusion, the sensitivity of the quadrupole coupling to chemical environment affords a useful check on theories of electron distribution in tungsten compounds and, combined with other techniques, gives a useful insight into tungsten chemistry.

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[34] We would like to thank D. A. J. Stone of the Department of Theoretical Chemistry, Cambridge for making available to us a version of this program. The original is described in ' Atomic Structure Calculations,' F. Hermann and S. Skillmann, Prentice Hall, Englewood Cliffs, 1963.

[35] E. A. Lucken, ' Nuclear Quadrupole Coupling Constants,' Academic Press, 1969, p. 315.