An Electron Spin Resonance Study of Bis(tetraphenylarsonium) Pentakis(isothiocyanato)nitrosyltechnetate(II): A Six-co-ordinate Low-spin $4d^5$ Technetium(II) Complex †

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The e.s.r. spectrum of the title complex has been studied in non-aqueous solution in the liquid and frozen glass phases. The spectrum is characteristic of a low-spin $4d^5$ technetium(II) ion in an axially symmetric environment with $g_{\parallel} = (+)\ 1.928$, $g_{\perp} = (+)\ 2.045$, $A_{\parallel} = 0.0236$, and $A_{\perp} = 0.0095\ \text{cm}^{-1}$. The small quadrupole interaction observed is solvent dependent. A simple crystal field model, in which the unpaired electron is located in the t_{2g} orbital triplet, is able to explain most features of the e.s.r. spectrum. A consideration of the electronic parameters derived from the g and A values leads to the conclusion that the results are best explained by a large tetragonal distortion from octahedral symmetry with strong π bonding between technetium and the ligands.

The use of the short-lived nuclide technetium-99m ($t_{\frac{1}{2}} = 6$ h, γ-energy 140 keV) in nuclear medicine has led to considerable interest in the chemical, structural, and spectroscopic properties of technetium compounds. The ready availability of the nuclide ^{99}Tc ($t_{\frac{1}{2}} = 2.12 \times 10^5$ years, β-energy *ca.* 0.3 MeV) enables conventional chemical studies to be performed. However, e.s.r. studies of ^{99}Tc compounds are still few in number, even though three valence states of technetium are odd-electron systems and hence paramagnetic, namely Tc^{VI} ($4d^1$), Tc^{IV} ($4d^3$), and the state of interest in this paper, Tc^{II} ($4d^5$). The first report of the e.s.r. spectrum of a technetium(II) complex was by Orvig *et al.*[1] who found that $[\text{NBu}^n{}_4][\text{Tc(NO)Br}_4]$ gave a ten-line hyperfine pattern in solution at room temperature, but supplied no further details. Yang *et al.*[2] recently reported the e.s.r. spectra of the ions *trans*-tetra-ammineaquanitrosyltechnetium(II) and pentachloronitrosyltechnetate(II) but did not analyse the spectral parameters in detail. The absence of detailed analyses may be contrasted with the situation for other low-spin d^5 ions, such as the $3d^5$ ions Fe^{III} and Mn^{II},[3] the $4d^5$ ion Ru^{III},[4,5] and the $5d^5$ ions Os^{III} [6,7] and Ir^{IV},[8] all of which have been extensively studied.

This paper reports the observation and analysis of the e.s.r. spectrum of the low-spin $4d^5$ complex, bis(tetraphenylarsonium) pentakis(isothiocyanato)nitrosyltechnetate(II), $[\text{AsPh}_4]_2[\text{Tc(NO)(NCS)}_5]$ in non-aqueous solutions.

Experimental

Ammonium (^{99}Tc)pertechnetate was supplied by Amersham International. Sodium (^{99m}Tc)pertechnetate (100 MBq, obtained from the Australian Atomic Energy Commission) was added to determine the chemical yield of the technetium compound. Kieselgel 60 (70—230 mesh) supplied by Merck (Darmstadt) was used for chromatography. Tetraphenylarsonium chloride was obtained from Fluka. All other reagents used were of analytical grade and were supplied by British Drug Houses. Distilled water was used throughout.

E.s.r. measurements were made at room temperature and at *ca.* 120 K using a Varian E-12 spectrometer operating at 9 139 MHz. The absorption spectrum in the u.v. and visible region was recorded on a Beckman Acta CII spectrophotometer and the i.r. spectrum was determined in a KBr disc on a Perkin-Elmer 197 spectrophotometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. ^{99m}Tc γ-activity was measured in a Capintec CRC-2N ionisation chamber.

Ammonium pertechnetate (2 cm^3, 56 mg Tc) was spiked with sodium (^{99m}Tc)pertechnetate (100 MBq) and the resulting solution taken to dryness. Isopropyl alcohol (10 cm^3) was added and the mixture again taken to dryness. The residue was dissolved in dimethylformamide (dmf) (20 cm^3) and hydroxylamine hydrochloride (1 g) and potassium thiocyanate (1.5 g) were added. The mixture was then heated in a boiling water-bath for 1 h during which time it gradually darkened. After cooling, water (50 cm^3) was added and the solution filtered. On adding a solution of tetraphenylarsonium chloride (0.5 mol dm^{-3}, 10 cm^3), a reddish blue precipitate containing 90% of the radioactivity formed and was collected by filtration, washed with water and diethyl ether, and allowed to dry. This precipitate was dissolved in dichloromethane, dried over anhydrous sodium sulphate, and applied to a silica gel column (2.5 cm diameter × 10 cm). A deep blue fraction (yield 45%) was eluted with dichloromethane and taken to dryness before further purification on a second silica gel column (1 cm diameter × 20 cm). Benzene was added to the blue dichloromethane fraction from this column and on concentration the solution deposited deep blue crystals which were collected by filtration, washed with benzene and diethyl ether, and dried under vacuum over P_2O_5, m.p. 304—306 °C (Found: C, 54.6; H, 3.50; N, 7.30; S, 13.6. $\text{C}_{53}\text{H}_{40}\text{As}_2\text{N}_6\text{OS}_5\text{Tc}$ requires C, 53.7; H, 3.40; N, 7.10; S, 13.5%). The i.r. spectrum showed peaks at 2 110m, 2 058s, 1 778s, 1 480m, 1 436m, 1 082m, 998m, 740m, and 688m cm^{-1}. No absorptions were observed in the region 760—1 050 cm^{-1}, confirming the absence of Tc=O.

E.S.R. Results and Interpretation.—A solution of $[\text{AsPh}_4]_2[\text{Tc(NO)(NCS)}_5]$ (1.0×10^{-3} mol dm^{-3}) in chloroform–dichloromethane (1 : 1 v/v) was an intense blue colour $\lambda_{\text{max.}}$ 546 nm (ε *ca.* 2×10^3 m^2 mol^{-1}) and at room temperature exhibited an e.s.r. spectrum consisting of ten approximately equally spaced lines, with an average splitting of 14.7 ± 0.3 mT, centred around $g = 2.020$. Such a spectrum is expected to arise from an ion with nuclear spin $I = \frac{9}{2}$ tumbling in solution. There was no evidence for additional splittings due to ligand superhyperfine interactions.

The e.s.r. spectrum of the above solution, frozen to 120 K, is shown in the Figure, and can be described in terms of the axially symmetric spin-Hamiltonian (1), where $S = \frac{1}{2}$, $I = \frac{9}{2}$, and the other terms have their usual meanings. There was no evidence for deviations from axial symmetry, nor for super-

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

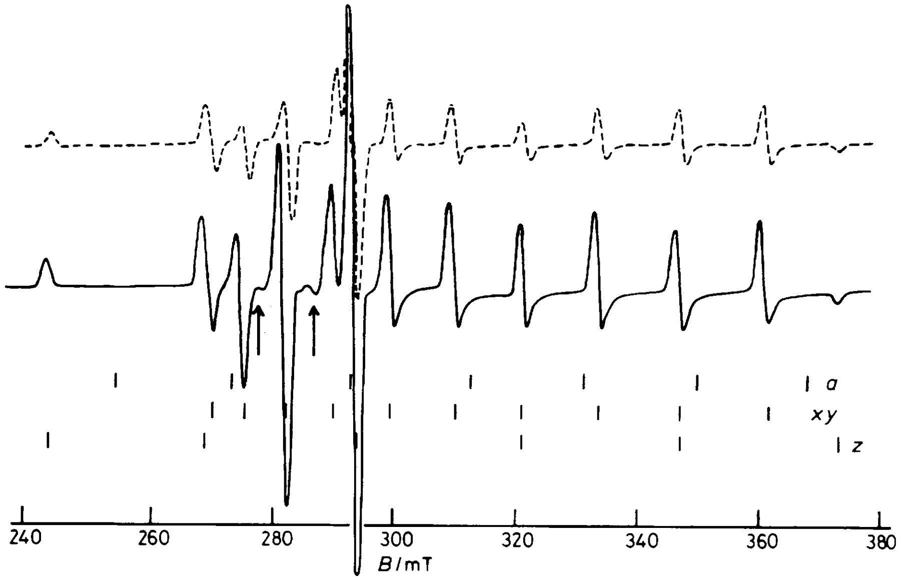

Figure. E.s.r. spectrum of $[AsPh_4]_2[Tc(NO)(NCS)_5]$ (1.0×10^{-3} mol dm^{-3}) in chloroform–dichloromethane (1 : 1 v/v) at 120 K and a microwave frequency of 9 139 MHz. The arrows indicate the positions of the weak resonances observed at *ca.* 280 and 288 mT attributed to the $\Delta m = \pm 1$ transitions. The broken line is a computer simulated spectrum for $\Delta m = 0$ using the parameters listed in Table 1 and a Gaussian lineshape, width 0.5 mT. The stick spectra relate to the parallel (*z* axis) and perpendicular (*xy* plane) directions as well as the direction corresponding to the angular anomaly (designated *a*). Not shown are four of the outermost features of the parallel spectrum which occur at 217.5, 402.5, 430.0, and 457.5 mT

$$\mathscr{H} = g_{\parallel}\beta B_zS_z + g_{\perp}\beta(B_xS_x + B_yS_y) + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) + Q[I_z^2 - \tfrac{1}{3}I(I + 1)] \quad (1)$$

hyperfine splittings arising from the interaction of the unpaired electron with the nitrogen nuclei of the nitrosyl or thiocyanate ligands. The spectrum was simulated as described by De Bolfo *et al.*[9] from the expressions for the magnetic fields and transition probabilities obtained by the use of second-order perturbation theory.[10] The best fit to the experimental spectrum was obtained when the quadrupole interaction term, $Q[I_z^2 - \frac{1}{3}I(I + 1)]$, was included in the Hamiltonian, and the appropriate parameters are given in Table 1. Although the spectrum covers a very large range of magnetic field, the second-order perturbation theory used here enabled the peak positions in the experimental spectrum to be fitted to better than 0.4 mT. In view of the probable errors in the measurement of the magnetic field, it was considered that computer diagonalization procedures were not necessary.

When $|Q| > 0$, forbidden transitions where $\Delta m = \pm 1$ or ± 2 may be observed in addition to the allowed $\Delta m = 0$ transitions. These forbidden transitions have an intensity proportional to Q^2 and their positions and relative intensities may be calculated from the parameters listed in Table 1 and the second-order perturbation theory expressions given by De Bolfo *et al.*[9,*]

It was found that the most intense resonance of the $\Delta m = \pm 1$ spectrum occurred at around 288 mT, with a less intense resonance at around 280 mT. Examination of the experimental spectrum at high spectrometer gain revealed resonances at these field positions, as shown in the Figure. Computer simulation of the spectrum due to the $\Delta m = \pm 2$ transitions showed that its most intense lines overlap with the most intense lines of the $\Delta m = 0$ transitions. As the former are very much less intense, they were not observed.

Table 1. E.s.r. spectral parameters for $[AsPh_4]_2[Tc(NO)(NCS)_5]$ [a]

$\langle g \rangle$ (solution)	2.020
$\langle A \rangle$ (solution)/cm^{-1}	0.0141
$g_{\parallel}$	1.928 ± 0.002
$g_{\perp}$	2.045 ± 0.002
$A_{\parallel}$/cm^{-1}	0.0236 ± 0.0003
$A_{\perp}$/cm^{-1}	0.0095 ± 0.0001
Q/cm^{-1}	0.0002 ± 0.000 05
	0.0001 ± 0.000 05 [b]

[a] In chloroform–dichloromethane (1 : 1 v/v). [b] Value in dmf and pyridine.

The intensities of the $\Delta m = \pm 1$ transitions are only about 1% of those of the $\Delta m = 0$ transitions. If both types of transition have the same linewidth (*ca.* 0.6 mT), this corresponds to $|Q| = (1.0 \pm 0.2) \times 10^{-4}$ cm^{-1}. The value of $|Q|$ obtained from a consideration of the line positions of the $\Delta m = 0$ transitions is $(2.0 \pm 0.5) \times 10^{-4}$ cm^{-1}. The reason for this discrepancy is not immediately obvious, but we feel that in view of the uncertainties in line-broadening mechanisms, the larger value is the more reliable. The positions of the $\Delta m = \pm 1$ transitions are effected very little by the magnitude of Q for values less than *ca.* 4.0×10^{-4} cm^{-1}.

The spectra observed in dmf and pyridine solutions were well resolved, and could be fitted with values of most parameters not significantly different from those used for the chloroform–dichloromethane (1 : 1 v/v) solvent mixture. The value of $|Q|$ for both dmf and pyridine solutions, calculated from the line positions of the $\Delta m = 0$ spectra, was 1.0×10^{-4} cm^{-1}: about 50% of that in chloroform–dichloromethane. Resonances were observed at *ca.* 288 mT in dmf and pyridine, but were less intense (*ca.* 20%) than in chloroform–dichloromethane.

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[*] There is a misprint in equation (6) of ref. 9, which should be as shown below.

$$\frac{I\,(\Delta m = \pm 2)}{I\,(\Delta m = 0)} = \left\{\frac{g_{\perp}{}^2A_{\perp}{}^2}{g^2K^2}\right\}^2\left\{\frac{P\sin^2\theta}{2K}\right\}^2[(I + 1)^2 - q^2](I^2 - q^2)$$

Table 2. Electronic parameters calculated using the simple crystal field model for $[AsPh_4]_2[Tc(NO)(NCS)_5]$ in chloroform–dichloromethane (1 : 1 v/v)

Parameter	Solution 1	Solution 2	Solution 3 [a]	Solution 4 [a]
$g_\parallel$	−1.928	+1.298	+1.928	−1.928
$g_\perp$	+2.045	+2.045	−2.045	−2.045
sign of ($g_\parallel \times g_\perp^2$)	−	+	+	−
a	0.5885	0.9916	(+) 0.9997	(+) 0.7300
b	0.8085	0.1293	(−) 0.0249	(−) 0.6834
k	1.003	0.218	57.9	2.205
P/cm^{-1}	0.361	0.0144	0.0169	0.0121
κ	3.42	1.24	0.792	−0.317
$\langle r^{-3}\rangle$/a.u. [b]	90.1	3.60	4.23	3.01
χ/a.u. [c]	−462	−6.69	−5.02	+1.43
η	0.0433	5.83	−27.9	0.407

[a] Note that the choice of sign for $g_\parallel$ and $g_\perp$ in these cases requires a and b to be of opposite sign. [b] 1 a.u. = 6.747×10^{30} m^{-3}. [c] 1 a.u. = 8.34 T.

The spectra observed in dimethyl sulphoxide, acetonitrile, and dichloromethane–benzene (1 : 3 v/v) were broader than in the other solvents, and did not lend themselves to as accurate a fit of their spectral parameters, although these were similar to those in the other solvents. The line broadening obscured any evidence for $\Delta m = \pm 1$ transitions, so that the presence of a small quadrupole interaction could not be confirmed.

Interpretation of Spin-Hamiltonian Parameters.—A consideration of the e.s.r. spectrum observed here shows that the ground state of the technetium(II) ion has $S = \frac{1}{2}$. If S was $\frac{3}{2}$ or $\frac{5}{2}$, either extra lines would be observed in the $g = 2$ region (*ca.* 326.0 mT) as was found for some Mn^{II} compounds [11] or, if the zero-field splitting parameters are large enough, in the $g = 6$ (*ca.* 110 mT) or $g = 4$ (*ca.* 150 mT) regions. Such resonances were not observed.

The theory of low-spin d^5 complexes has been discussed by a number of authors.[3–8,12–18] Provided that the electron spin-coupling energy is smaller than the crystal field energy and that the crystal field has octahedral symmetry, all five d electrons are located in the orbital triplet (labelled as t_{2g}) which is located an energy Δ below the orbital doublet e_g. For the free ion, this requires $\Delta/B > ca.$ 30, where B is the Racah parameter. The simplest treatment of this situation is that of Bleaney and O'Brien,[12] who consider only interactions within the triplet states, so that the system is taken to be a single hole in the t_{2g} shell. More recent analyses have considered the effects of the e_g orbitals and of covalent bonding.[6–8,17]

The symmetry of the complex and the ground-state wavefunctions. The wavefunctions of the ground state are determined by the symmetry of the crystal field around the technetium(II) ion. Whilst an axially symmetric e.s.r. spectrum can arise from either a tetragonal or a trigonal distortion of the octahedral crystal field if all six ligands are identical, the nitrosyl ligand in $[Tc(NO)(NCS)_5]^{2-}$ imposes tetragonal symmetry. The tetragonal distortion is assumed to be along the Tc–NO bond direction, which is defined as the z axis. The wavefunctions of the t_{2g} orbital triplet can then be written in the conventional manner as combinations of the one-electron states labelled as $|xy\rangle$, $|yz\rangle$, and $|xz\rangle$, and the wavefunction of the ground-state orbital singlet is written as equations (2) and (3), and a and b are related by equation (4).[18]

$$|+\rangle = -\frac{ia}{\sqrt{2}}(|\overset{+}{2}\rangle - |-\overset{+}{2}\rangle) + ib|-\overset{-}{1}\rangle \tag{2}$$

$$|-\rangle = -\frac{ia}{\sqrt{2}}(|\overset{-}{2}\rangle - |-\overset{-}{2}\rangle) - ib|\overset{+}{1}\rangle \tag{3}$$

$$a^2 + b^2 = 1 \tag{4}$$

It is important to note that the wavefunctions (2) and (3) obey time reversal symmetry, as required by a consistent Kramers' doublet, *i.e.* $\theta|+\rangle = |-\rangle$ and $\theta|-\rangle = -|+\rangle$, where θ is the time reversal operator.[19] If the wavefunctions do not obey time reversal, sign inconsistencies may arise in the interpretation of the g and hyperfine values.[20] For example, the wavefunctions labelled as $|+\rangle$ and $|-\rangle$ by Bleaney and O'Brien [12] do not obey time reversal and lead to opposite signs for g and A to those given below.

The g *values.* These are obtained by applying the magnetic moment operator $k\hat{L} + g_e\hat{S}$ to the states $|+\rangle$ and $|-\rangle$; k is the so-called orbital reduction factor which is expected to be < 1. The decrease of k from unity is regarded as a measure of the covalency, *i.e.* the amount of π bonding (see, for example, Griffiths *et al.*[14]). However, values of $k > 1$ are possible if configuration interactions with the excited states are present, as discussed by Bohan; [16] g_e is the free-electron g value, *i.e.* 2.0023. The expressions for the g values in terms of k, g_e, and the coefficients of the wavefunctions are given by (5) and (6).

$$g_\parallel = g_e(a^2 - b^2) - 2kb^2 \tag{5}$$

$$g_\perp = g_e a^2 + 2\sqrt{2}(kab) \tag{6}$$

From equations (4)—(6) it is apparent that if k is unrestricted and a and b are real, both $g_\parallel$ and $g_\perp$ may be either positive or negative. There are thus four sets of values for a, b, and k which may fit the results since the signs of $g_\parallel$ and $g_\perp$ cannot be determined in our experiment. In the present case there is no *a priori* reason why one particular set of signs of the g values should be favoured and the four possible sets of solutions of (4)—(6) are given in Table 2. One possible approach to deciding which solution is appropriate is to follow De Simone [15] and use the values of a and b and the measured values of the hyperfine interaction constants $A_\parallel$ and $A_\perp$ to calculate the hyperfine parameters P and κ for each set. We may then decide which set gives physically reasonable values.

The hyperfine parameters. For the present case of a tetragonal distortion along the z axis the application of the hyperfine structure operator (7) to the wavefunctions (2) and (3) gives equation (8). Expressions equivalent to (7) for the x and

$$N_Z = 2P\{L_Z + (\tfrac{4}{7} - \kappa)S_Z - \tfrac{1}{7}[L_Z(\hat{L}\cdot\hat{S}) + (\hat{L}\cdot\hat{S})L_Z]\} \tag{7}$$

$$A_\parallel = 2P\left[-\frac{2}{7} - \frac{6b^2}{7} + \frac{6ab}{7\sqrt{2}} + \frac{\kappa}{2}(b^2 - a^2)\right] \tag{8}$$

$$A_\perp = 2P\left(\frac{a^2}{7} + \frac{11ab}{7\sqrt{2}} - \frac{\kappa a^2}{2}\right) \tag{9}$$

y directions give equation (9). As pointed out by Bleaney and O'Brien,[12] different expressions arise if the symmetry of the crystal field is other than tetragonal.

The unknown constants κ and P can be obtained from the measured hyperfine splittings and the values of a and b calculated previously. The parameter κ arises from the Fermi contact term and is both dimensionless and positive, whilst P is given by equation (10) where g_e, g_n, β, and β_n have their

$$P = g_e g_n \beta \beta_n \langle r^{-3} \rangle \qquad (10)$$

usual meanings and $\langle r^{-3} \rangle$ represents the mean inverse cube radius of the unpaired electron from the nucleus. The reduction of P and hence of $\langle r^{-3} \rangle$ in the bound ion indicates the degree of covalency.

The values of κ and $\langle r^{-3} \rangle$ may be used to calculate another parameter, χ, where $\kappa \langle r^{-3} \rangle = -\frac{2}{3}\chi$. The parameter χ is related to the magnetic field at the nucleus due to core polarization [21] and has been calculated theoretically.[22]

In a simple resonance experiment, the signs of $A_\parallel$ and $A_\perp$ cannot be determined. However, an analysis of the solution spectrum shows that they must have the same sign.[23] The values of κ, $\langle r^{-3} \rangle$, and χ are given in Table 2. Since g_n is positive, P must be positive, and this requires that both $A_\parallel$ and $A_\perp$ are negative. The calculation of κ is not affected by the sign of the hyperfine constants.

A comparison of the values of $\langle r^{-3} \rangle$ and χ given in Table 2 with the free-ion values of 5.015 a.u. and −8.81 a.u. respectively [22] shows that only those values corresponding to solutions 2 and 3 are reasonable. As we shall see below, solution 2 is the only one to give a consistent set of parameters.

Whilst the value of $\kappa = 1.24$ given by solution 2 appears large (by comparison, values of κ for $3d^5$ low-spin Mn^{2+} ions [12] may be *ca.* 0.3—0.5), the corresponding value of P is reduced by only 25% from the free-ion value of 0.0201 cm^{-1}. The value of κ implies that the s electron density at the technetium nucleus is much larger than that for similar manganese complexes. This may be expected because of the differences in the spatial relationships between the s and d electron wavefunctions in the two cases.[22]

The quadrupole interaction. The nuclear quadrupole moments of the ^{99}Tc and ^{55}Mn nuclei are $-0.19(5) \times 10^{-28}$ and 0.35×10^{-28} m^2 respectively.[24,25] It would therefore be expected that the e.s.r. spectrum of a technetium(II) compound would exhibit a quadrupole splitting approximately one third that of an analogous manganese(II) compound. The quadrupole interaction constant of the spin-Hamiltonian, Q in equation (1), for technetium(II) in $[Tc(NO)(NCS)_5]^{2-}$ is found to be *ca.* 0.0002 cm^{-1} whereas $Q = 0.0020$ cm^{-1} was found for manganese(II) in the analogous compound $Na_2[Mn(NO)(CN)_5]$.[25] A possibly related observation is that by Griffiths and Owen [26] who were unable to detect a quadrupole interaction in certain Ir^{IV} complexes, even though the nuclear quadrupole moments of the relevant Ir^{IV} nuclei are some four times larger than that of ^{55}Mn. They [26] suggest that the ligand contribution to the electric field gradient at the nucleus is of approximately equal magnitude but of opposite sign to that produced by the unpaired d electron. A similar explanation may hold in the present case.

The splitting of the t_{2g} states. By applying the Hamiltonian of the crystal field and the spin–orbit coupling to the wavefunctions of the states of the orbital triplet, we obtain the secular equations which can be used to determine the tetragonal splitting δ in terms of the spin–orbit coupling parameter λ.[18] Equation (11) may be used to calculate η from the values of a and b given in Table 2.

$$\eta = \frac{\delta}{\lambda} = \frac{a}{b\sqrt{2}} - \frac{b}{a\sqrt{2}} + \frac{1}{2} \qquad (11)$$

It can be seen that solution 2 is the only one which gives a physically meaningful result, since the negative sign of solution 3 implies that the hole is largely in the d_{xz} or d_{yz} orbital, which contradicts the original calculation of a and b whereby the large value of a implies that the hole is largely in the d_{xy} orbital. We have already seen that solutions 1 and 4 are unacceptable because of the values of the hyperfine parameters which result, so that we may conclude that the hole is largely in the d_{xy} orbital with a large tetragonal field splitting of the other orbitals of the triplet. Using $\lambda = 950$ cm^{-1} (this is the free-ion value and the actual value of λ will be reduced somewhat due to covalency: see below), we obtain a splitting of *ca.* 4 000 cm^{-1}.

The conclusion that the tetragonal splitting is large is opposite to that reached by Yang *et al.*[2] for the ions $[Tc^{II}(NH_3)_4(NO)(H_2O)]^{3+}$ and $[Tc^{II}(NO)Cl_5]^{2-}$, but these authors did not analyse their g and hyperfine values in any detail.

Estimates of contributions from the excited states. Whilst most of the parameters resulting from solution 2 appear to be reasonable, the low value of k indicates that the simple crystal field model used so far may be inadequate. It can be shown that for both $g_\parallel$ and $g_\perp > 0$, k varies very rapidly as $g_\parallel$ approaches g_e from below and tends to infinity as $g_\parallel \rightarrow g_e$. This means that small changes in the coefficients of the wavefunctions, namely a and b, have a dramatic effect on k, even though the parameters derived from the hyperfine interaction, namely κ, $\langle r^{-3} \rangle$, and χ are not so dramatically affected. Thus the wavefunctions of the ground state must also include admixtures of excited states and as pointed out by Thornley,[8] the mechanisms giving rise to these are spin–orbit coupling, electrostatic interactions, and the admixture *via* spin–orbit coupling of charge-transfer configurations as a result of covalency. Thornley [8] used first-order perturbation theory to derive expressions for the corrections to the g and hyperfine interaction constants for the octahedral halide complexes of Ir^{IV} and showed that these corrections could affect significantly the estimates of k and the covalency parameter. Unfortunately the analysis of Thornley requires the use of additional experimental data which is not available in the present case. A further consideration is that the perturbation theory treatment used by Thornley may not be adequate when the tetragonal crystal field splitting is as large as in the present case.

Somewhat simpler calculations, ignoring charge-transfer effects, have been performed by Hill,[6] Sakaki *et al.*,[7] and Sato *et al.*[17] and have given expressions for the corrections to the g values in terms of the spin–orbit coupling constant, the orbital reduction factor, and the excited state energies. The latter involve the octahedral field splitting, Δ, and the Racah parameters B and C. If the spin–orbit coupling is larger than the electrostatic interactions (*i.e.*, $\lambda > B$), as is the case here and in general for other $4d^5$ and $5d^5$ ions (but is not the case for the $3d^5$ ions considered by Sato *et al.*[17]), the expressions of Sato *et al.*[17] may be approximated by those of Hill [6] and Sakaki *et al.*[7] The corrections to the g values may then be estimated using the following additional information. (*i*) The octahedral field splitting, Δ, is determined from the absorption maximum at 546 nm to be 18 300 cm^{-1}. (*ii*) From Griffith [27] (see also Wendlandt *et al.*[24]) the free-ion Racah parameter, B_0, is estimated to be 500 cm^{-1}. (*iii*) Solution 2 (Table 2) gives $\langle r^{-3} \rangle = 3.60$ a.u., which may be compared with the free-ion value of 5.015 a.u.[28] Since the spin–orbit coupling constant, λ, is approximately proportional to $\langle r^{-3} \rangle$,[29] the values of λ and B for the bound technetium(II) ion are $\lambda = 682$ cm^{-1} ($\lambda_0 = 950$ cm^{-1}) [27] and $B = 258$ cm^{-1} [note that $B/B_0 = (\lambda/\lambda_0)^2$; see Sato *et al.*[17]].

These assumptions give $\Delta/B = ca.$ 70, which is similar to the values for some ruthenium(III) complexes.[6,7] Values of $\Delta/B = ca.$ 35 are usually assumed for the low-spin complexes of the $3d^5$ ions manganese(II) and iron(III), whilst Sakaki *et al.*[7] and Thornley[8] have used values of $\Delta/B = 60$ or greater for the $5d^5$ low-spin ions osmium(III) and iridium(IV). Thus the estimate of B and the identification of the absorption at 546 nm as being due to the *d–d* transition seems reasonable.

In the notation of equations (2)—(7), for the case of axial symmetry, the corrections to the g values are given[6,7] by equations (12) and (13); k is the apparent orbital reduction factor, calculated earlier using equations (4)—(6) and is related to an average orbital reduction factor, K, by equation (14).

$$\delta g_{\parallel} = [2\lambda_0/\Delta][k/(1 + 12B/\Delta)]^2[4a^2 - 2\sqrt{2}(ab)] \quad (12)$$

$$\delta g_{\perp} = [2\lambda_0/\Delta][k/(1 + 12B/\Delta)]^2[b^2 - \sqrt{2}(ab)] \quad (13)$$

$$k = (1 - 12B/\Delta)K \quad (14)$$

If the original value of k, namely 0.218, is used in these expressions, a, b, and the hyperfine parameters are not significantly different to those found originally and η is reduced only from 5.83 to 5.44. However, k may be estimated also from the reduction in the spin–orbit coupling parameter which has been determined from the reduction in $\langle r^{-3}\rangle$. This gives $K = 0.718$ and hence the 'triplet only' orbital reduction factor k is 0.839. These values are certainly more in accord with expectation, but if they are used in the expressions of Sakaki *et al.*[7] it leads to physically meaningless solutions.

In a similar manner, the more complete expressions of Sato *et al.*[17] involving both spin–orbit and electrostatic admixtures, do not lead to satisfactory results and it appears therefore that the present theory for calculating the corrections is inadequate in this particular case.

Discussion and Conclusions

In general, the inability of a simple e.s.r. experiment to determine uniquely the signs of the electronic g values leads to ambiguities in the interpretation of the spectra of low-spin d^5 ions. In the present case, a consideration of the parameters derived from the hyperfine interaction has enabled us to decide in favour of the solution where both $g_{\parallel}$ and $g_{\perp}$ are positive, *i.e.* the product $(g_xg_yg_z) > 0$. As can be seen from Table 2 and from the results of other authors, the correct choice of sign for the g values is essential if the description of the ion in terms of orbital admixture and crystal field splitting is to be valid. The choice of sign for the g values cannot always be made using the value of the apparent orbital reduction factor, k, and often requires additional measurements such as magnetic susceptibility, Mössbauer effect, or measurements of the e.s.r. hyperfine interaction parameters.

In the context of the strong covalent π bonding to the ligands implied by the large crystal field splitting, it is surprising that no superhyperfine structure due to either the thiocyanate or nitrosyl nitrogen atoms was observed. The linewidths here were small enough to allow the observation of an interaction of the same magnitude as that of *ca.* 0.5 mT observed for the nitrosyl nitrogen atom in $Na_2[Mn(NO)(CN)_5]$.[25] However, the absence of nitrogen superhyperfine structure does not exclude N-bonding of the thiocyanato-ligands, as a similar absence of nitrogen superhyperfine structure arises in 3,10,17,24-tetrasulphonatophthalocyaninatomanganate(4−) where the manganese(II) ion is co-ordinated directly to the nitrogen atoms of the ligand.[30] Whilst Orvig *et al.*[1] suggested the N-bonded isothiocyanato-structure for $[NBu^n{}_4]_2[Tc(NO)(NCS)_5]$, they were unable to establish the mode of bonding. Our e.s.r. results cannot distinguish between N- and S-bonding to the technetium atom and the question can best be resolved by an *X*-ray structural analysis.

Acknowledgements

We would like to thank Dr. J. R. Pilbrow, Physics Department, Monash University, for the use of the Varian E-12 e.s.r. spectrometer.

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Received 23rd June 1983; Paper 3/1075