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Structural relationships derived from the analysis of electron spin resonance spectra of some technetium complexes

J. Barrie Raynor*
Department of Chemistry, University of Leicester, Leicester LE1 7RH (UK)

Terence J. Kemp and Aubrey M. Thyer
Department of Chemistry, University of Warwick, Coventry CV4 7AL (UK)

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Abstract

An extension of a method relating chemical structure to the ESR parameters $A_\parallel$ and $g_\parallel$ of paramagnetic technetium complexes is presented. Complexes having the same axial ligand lie in a narrow band of values of $A_\parallel$ and $g_\parallel$ such that Tc(II) nitrosyl and thionitrosyl complexes have distinctly different ESR parameters to Tc(VI) nitrido and oxo complexes. Thus the ESR spectrum of a solution resulting from a reaction where the nature of the product is in some doubt can be used to identify the oxidation state, the nature of the axial ligand and possible equatorial ligands.

Introduction

Technetium has a wide ranging chemistry in solution. A major problem in studying and characterising technetium compounds and species in solution is the small scale, and dilution, required in their study because of its cost and radioactivity, albeit of low energy. The longest lived isotope, ^{99}Tc, has a half life of 2.14×10^5 years. Compounds of technetium have oxidation states ranging from +7 to +1 in aqueous solution, in which oxidation states can readily change and are subtly dependent on reaction conditions.

Fortunately, technetium compounds with oxidation states VI and II (d^1 and d^5) are readily detected by electron spin resonance spectroscopy (ESR) and reactions can often be followed by this technique. The radioactivity of technetium solutions makes ESR spectroscopy a particularly appropriate technique for their study since only very small concentrations are needed. In the course of our studies on aspects of the chemistry of technetium which have involved a range of reducing reagents such as hydrazine and nitric oxide, characterisation of species in solution has been considerably aided by analysis of their ESR spectra. Unfortunately, in some cases ambiguity in characterisation still remained. This prompted us to investigate the relationship between the ESR parameters of established technetium complexes and their ligand coordination.

This approach has resulted in the development of graphical relationships in which $g_\parallel$ and $A_\parallel$ (Tc) are found to depend dramatically upon the nature of the coordinating atoms. This is, perhaps, not surprising since the ESR parameters themselves are dependent upon the relative energies of the molecular orbitals and their bonding coefficients. In this paper, we derive relationships between the ESR parameters and coordinating ligands for a series of –O, –N, –NO, –NS complexes of Tc(VI) and Tc(II).

Technetium(VI) (d^1) complexes

Nitrido complexes of Tc are well known with the halide ligands F, Cl and Br [1–5]. In most cases, there is no evidence for a sixth axial ligand, and the complex anions are thus formulated $[TcNX_4]^-$, $X = F^-$, Cl^-, Br^-, although Kirmse *et al.* [4] have presented evidence for a $[TcNCl_5]^{2-}$ ion. Only one oxo complex anion is known, $[TcOCl_5]^-$, although evidence for the presence of the fifth Cl is ambiguous [6].

In all complexes, the unpaired electron is in an orbital of $b_2(d_{xy})$ symmetry (C_{4v}). Calculation of the bonding parameters are fraught with difficulty because of assumptions needed for certain values. Thus Kon and Sharpless [7] have calculated molecular orbital coefficients using the standard second-order perturbation theory of Abragram and Pryce [8], but it assumes

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*Author to whom correspondence should be addressed.

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knowledge of the energies of the transitions $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{xz,yz}$ as well as overlap integrals, $\langle r^{-3} \rangle$, spin orbit coupling constants and the Fermi contact term. Alternatively, McGarvey [9] has provided simpler expressions involving only an assumption for the value of P ($P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$) which requires knowledge of the expectation value $\langle r^{-3} \rangle$ for the electron density in the $4d_{xy}$ orbital of Tc. Kivelson and Neiman [10] have shown that $g_\parallel$ and $g_\perp$ decrease, and $A_\parallel$ and $A_\perp$ increase with increasing covalency between the metal and equatorial ligands in a d^9 system with a b_1 ground state ($d_{x^2-y^2}$).

For the d^1 case with the unpaired electron in a $b_2(C_{4v})$ ground state, the molecular orbital is of the form

$$B_2 = \beta_2^* d_{xy} - \beta_2^{*\prime}(p_y^1 + p_x^2 - p_y^3 - p_x^4)/2 \qquad (1)$$

where the four equatorial ligands are placed on the $\pm x$ and $\pm y$ axes and are labelled by the superscripts. g values are given by the expressions

$$g_\parallel = g_0 - \frac{8\beta_1^{*2}\beta_2^2\xi}{\Delta E_1} + \frac{8\beta_1^2\beta_2^2\xi}{\Delta E_1'} \qquad (2)$$

$$g_\perp = g_0 - \frac{2\beta_2^2 e^2 \xi}{\Delta E_2} + \frac{2\beta_2^2 e^{*2}\xi}{\Delta E_2'} \qquad (3)$$

where ξ is the spin orbit coupling constant to the Tc(VI) ion. ΔE is defined in the partial energy diagram in Fig. 1. Further consideration to these equations will be given later.

The hyperfine coupling to Tc is given by the expressions

$$A_\parallel = -K - \frac{4\beta_2^{*2}P}{7} - (g_0 - g_\parallel)P - \frac{3(g_0 - g_\perp)P}{7} \qquad (4)$$

$$A_\perp = -K - \frac{2\beta_2^{*2}P}{7} - \frac{11(g_0 - g_\perp)P}{14} \qquad (5)$$

in both cases, neglecting further small terms.

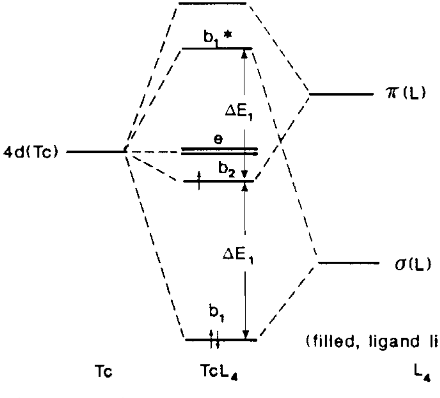

Fig. 1. Partial energy level diagram for Tc(VI) (d^1) complexes (C_{4v}) showing the orbitals involved in bonding to equatorial ligands.

Since

$$g_{av} = (g_\parallel + 2g_\perp)/3 \qquad (6)$$

and

$$A_{av} = (A_\parallel + 2A_\perp)/3 \qquad (7)$$

then eqn. (4) can be rearranged as

$$A_\parallel = -K - \frac{-4\beta_2^{*2}P}{7} + \frac{11P(g_\parallel - g_{av})}{14} \qquad (8)$$

This expression does not involve defining $g_\parallel$ and $g_\perp$ as in eqns. (2) and (3) and hence it is unnecessary to attempt to evaluate either β_1^{*2} and e_π^{*2} or the energy gaps ΔE.

In these equations, $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$, where $\langle r^{-3} \rangle$ is the value of the $4d_{xy}$ electron density radial function for the technetium ion and $K = \kappa\beta_2^2 P$, where κ is the Fermi isotropic interaction constant. Provided that P can be estimated, β_2^2 can be calculated, but this assumes usually that P is a constant. Some workers consider that there is an effective charge transfer from ligand to metal of two electrons and use a value of $P = 0.0245$ cm^{-1} appropriate to the Tc(IV) ion [1].

The most significant terms in this relationship (eqn. (8)) are $A_\parallel$ and $g_\parallel$. A plot of known data (Table 1) for d^1 complexes of Tc is given in Fig. 2. The roughly linear relationship for the nitrido complexes shows that the variation in κ, β_2^2 and g_{av} is small and that overall they largely cancel each other out.

The correlation involving $g_\parallel$ is interesting also in that $g_\parallel$ itself is made up of two important terms which themselves are variables. These equations ((2) and (3)) are based on second order perturbation theory involving mixing of the ground state orbital $b_2(d_{xy})$ with orbitals of symmetry b_1 which are higher in energy (b_1^*) and lower, filled, b_1 as shown in the partial energy level diagram in Fig. 1. The energies $\Delta E_1 = b_1^* - b_2$ and $\Delta E_1' = b_2 - b_1$. In eqn. (3) $\Delta E_2 = e^* - b_2$ and $\Delta E_2' = b_2 - e$. ξ is the free ion spin orbit coupling constant for Tc(VI).

Since the terms involving β_1, β_2 and e in eqns. (2) and (3) are opposite in sign, then whether $g_\parallel$ is > or < 2 depends on, among other things, the relative energy gaps between b_2 and the upper and lower b_1^* and b_1 orbitals. The stronger the π-bonding between Tc and the equatorial ligands, the lower in energy b_2 becomes and the smaller is $\Delta E_1'$. Thus the second term may become larger than the first. This is clearly seen for the nitrido complexes with halogen ligands whereby $g_\parallel$ varies as Br > Cl > F. π-bonding strength decreases in this order with Br largest because of the close proximity in size of the $4d_{xy}$ and the 4p orbitals on Br. This effect is well established for the oxyhalides of Cr and Mo [12–14].

TABLE 1. ESR spin Hamiltonian parameters for Tc(VI), d^1, complexes (hyperfine splittings $\times 10^{-4}$ cm^{-1})

No.	Complex	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	Reference
1	$[TcNF_4]^-$ in HF	1.895	1.990	377	179	1
2	$[TcNCl_4]$ in HCl	2.0075	2.002	295	134	2, 3
3	$[TcNCl_5]^{2-}$ in $CHCl_3$	2.016	2.003	295	137	4
4	$[TcNCl_4]^-$ in $CHCl_3$	2.008	(2.000)	293	(134)	5
5	$[TcNBrCl_3]^-$ in CH_3CN	2.046	(2.007)	280	(133)	5
6	$[TcNBr_2Cl_2]^-$ in CH_3CN	2.076	(2.022)	268	(132)	5
7	$[TcNBr_3Cl]^-$ in CH_3CN	2.115	(2.031)	258	(128)	5
8	$[TcNBr_4]$ in HBr	2.145	2.032	249	120	2, 3
9	$[TcNBr_4]^-$ in CH_3CN	2.147	(2.036)	248	(121)	5
10	$[TcNCl_3(CN)]^-$	2.013	2.006	277	127	11
11	$[TcNCl_2(CN)_2]^-$	2.018	1.998	261	115	11
12	$[TcOCl_5]^-$ in HCl	2.057	1.938	230	96	6

Numbers in brackets were computed from isotropic measurements.

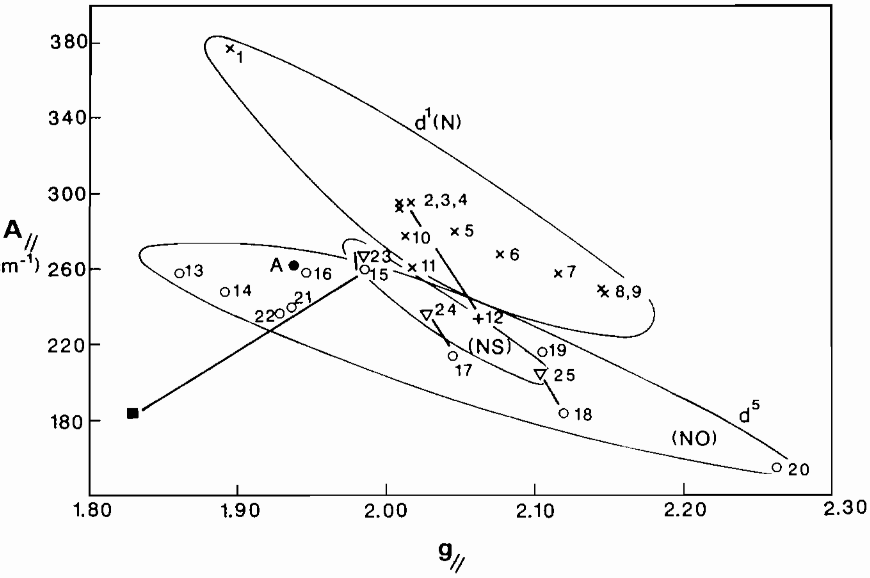

Fig. 2. Correlation between $g_\parallel$ and $A_\parallel$ for Tc(VI) (d^1) and Tc(II) (d^5) complexes. Complexes are identified by number which correspond to the numbers in Tables 1 and 2. The enclosures collect together the sets of data d^1 (N), d^5 (NO) and d^5 (NS). The solid lines link together pairs of complexes where the only variable is the axial ligand, viz. complexes 2, 3, 4–12 $[Tc(O/N)Cl_5]^{n-}$, 15–23 $[Tc(NO/NS)Cl_5]^{2-}$, 17–24 $Tc(NO/NS)Cl_3P_2]$ and 18–25 $[Tc(NO/NS)Br_3P_2]$. ○ = $[Tc(NO)L_n]$ (13–22), ∆ = $[Tc(NS)L_n]$ (23–25), + = $[TcOCl_5]^-$ (12), × = $[TcNL_n]$ (1–11), ■ = $[Tc_2Cl_8]^{3-}$. 'A' indicates the parameters of the solution from the reaction described in the text.

In the case of $[TcOCl_5]^-$, $g_\parallel$ is close to that for $[TcNCl_5]^{2-}$, (2.057 and 2.016, respectively), but $A_\parallel$ is significantly smaller (230×10^{-4} compared with 295×10^{-4} cm^{-1}, respectively). The change in $A_\parallel$ can readily be accounted for in terms of eqns. (4) or (8) since $g_\perp$ will be very sensitive to π-bonding between Tc and O or N along the z-axis. Referring to eqn. (3) for $g_\perp$, the value of $g_\perp$ for $[TcOCl_5]^-$ is normal and as expected, viz. less than 2.0. However, with the nitrido complex, there will be a much stronger bond between the Tc and the N which will stabilise the bonding e orbital and destabilise the antibonding e* orbital (Fig. 3). Thus $\Delta E_2'$ and ΔE_3 are larger and the second and third terms in eqn. (3) diminish in significance with the result that $g_\perp$ is closer to g_0 for the nitrido complex. Because the third term in eqn. (8) is of opposite sign to that of the first two, then the smaller value of $g_\perp$ for the oxo complex has a larger influence on the term in the nitrido complex, and contributes markedly to making $A_\parallel$ less negative and so a smaller absolute value. In Fig. 2, a line is drawn linking the results for this pair of complexes (numbers 2, 3 and 4 with 12).

Technetium(II) (d^5) complexes

Paramagnetic complexes of Tc(II) almost always have nitrosyl or thionitrosyl as an axial ligand. The presence

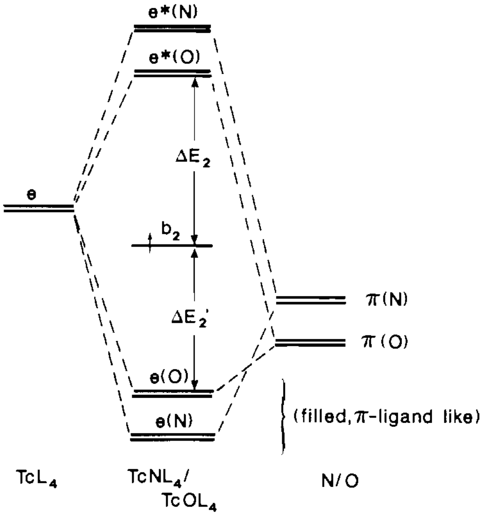

Fig. 3. Partial energy level diagram for Tc(VI) complexes (C_{4v}) showing the influence of π-bonding to axial O and N atoms.

of these strongly bonded ligands is such as to give the Tc(II) an $e^4b_2^1$ outer electron configuration, with the NO nominally as NO^+. The basic molecular orbital energy level diagram is similar to that for d^1 complexes (Fig. 1) except that the energy of the e and b_2 levels are reversed. Since the ground state is the same, then we can use the same equations as given for the d^1 system. It follows that the same sort of trends would be expected. A plot of known data (Table 2) is given in Fig. 2.

The trend in parameters for nitrosyl complexes is very similar to that found for d^1 complexes. Complexes having most π-bonding between the Tc and equatorial ligands possess the largest $g_{\|}$ and the smallest $A_{\|}$ (e.g. $[Tc(NO)I_5]^{2-}$). At the other extreme, $[Tc(NO)(H_2O)(NH_3)_4]^{3+}$, with no π-bonding in the equatorial plane, has the smallest $g_{\|}$. There are two reports of parameters for $[Tc(NO)Cl_5]^{2-}$ with rather widely differing $g_{\|}$ values. Inspection of Fig. 2 suggests that the results of Yang *et al.* [15] are wrong since the other results by Kirmse *et al.* [16] fall nicely on a line with the corresponding bromo and iodo complexes (compounds 15, 19, 20).

A few simple complexes exist which involve the thionitrosyl axial ligand. Fortunately, corresponding nitrosyl complexes exist for three of them and so a useful comparison can be made. In all cases, the nitrosyl complex has a lower $A_{\|}$. The reason for this is the increase in backbonding between Tc and NO compared with Tc and NS thus making the Tc–NO bond stronger than Tc–NS. This stabilises the filled bonding e orbital (formerly non-bonding) and stabilises the antibonding e* orbital (Fig. 4). The effect follows the same logic as outlined above for the $[TcOCl_5]/[TcNCl_5]^{2-}$ comparison. In Fig. 2, lines are drawn which link the thionitrosyl and corresponding nitrosyl complexes to emphasise this relationship.

An interesting extension to this is to consider the dimer $[Tc_2Cl_8]^{3-}$ which can be considered as a $[Tc(III)Cl_4]^-$ unit bonded to $[Tc(II)Cl_4]^{2-}$ by a Tc–Tc bond of order 3.5 [23]. By comparison with $[Tc(NO)Cl_5]^{2-}$, both $g_{\|}$ and $A_{\|}$ are significantly lower. $[Tc(III)Cl_4]^-$ effectively replaces NO in the axial position. The increase in the Tc–Tc bond strength in the dimer further depresses the energy of the filled e bonding orbitals and creates the opportunity for both $g_{\|}$ and $A_{\|}$ to be lower than for nitrosyl complexes.

Correlations of the sort described above are well established for d^1 $(VO)^{2+}$ [24–26] and d^9 (Cu^{2+}) [10, 27, 28] complexes, and are based on equations devised by Kivelson and Neiman [10] McGarvey [9] and others [29, 30].

Their value lies in their qualitative usefulness as predictors of structure or oxidation state in chemical systems in which there is doubt. Despite the many variables, the correlations are clearly useful.

TABLE 2. ESR spin Hamiltonian parameters for Tc(II), d^5, complexes (hyperfine splittings $\times 10^{-4}$ cm^{-1})

No.	Complex[a]	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$	Reference
13	$[Tc(NO)(H_2O)(NH_3)_4]^{3+}$	1.861	2.114	258	108	15
14	$[Tc(NO)Cl_5]^{2-}$	1.891	2.104	248	107	15
15	$[Tc(NO)Cl_5]^{2-}$	1.985	2.037	260	111	16
16	$[Tc(NO)Cl_3(pd)]^-$	1.946	2.017	258	105	17
17	$[Tc(NO)Cl_3P_2]$	2.045	2.049	214	89	18, 19
18	$[Tc(NO)Br_3P_2]$	2.119	2.100	184	79	18
19	$[Tc(NO)Br_4]^-$	2.105	2.081	216	89	16
20	$[Tc(NO)I_4]^-$	2.262	2.144	155	73	20
21	$[Tc(NO)(NCS)_5]^{2-}$	1.936	2.042	240	99	16
22	$[Tc(NO)(NCS)_5]^{2-}$	1.928	2.045	236	95	21
23	$[Tc(NS)Cl_5]^{2-}$	1.984	2.041	266	119	22
24	$[Tc(NS)Cl_3P_2]$	2.027	2.039	237	106	18
25	$[Tc(NS)Br_3P_2]$	2.103	2.078	205	94	18

[a] pd = 2,4-pentanedione; P = (Me_2PhP).

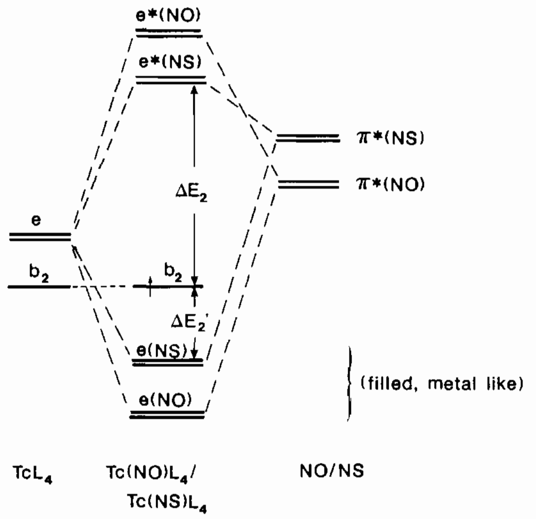

Fig. 4. Partial energy level diagram for Tc(II) complexes (C_{4v}) showing the influence of π-bonding to the axial NO and NS ligands.

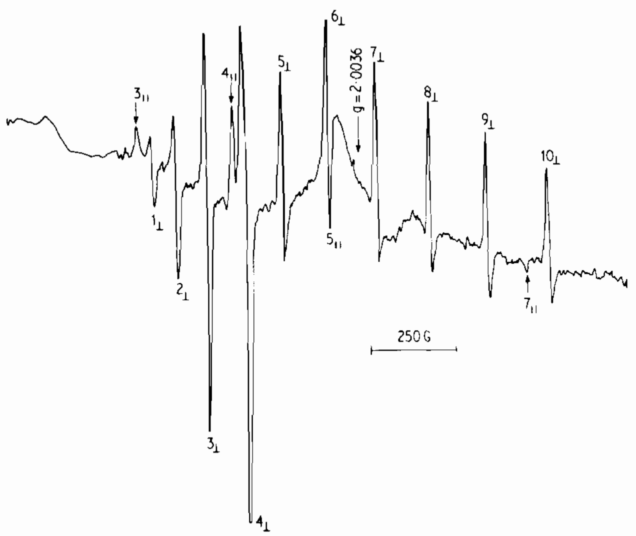

Fig. 5. ESR spectrum at 77 K of species A given by the n-butyl acetate extract from a solution of $HClO_4$ (6.0 mol dm^{-3}), TcO_4^- (1.6×10^{-3} mol dm^{-3}) and hydrazine (0.2 mol dm^{-3}) on bubbling with NO during the 'fast stage' of evolution of N_2.

Illustrative of this approach is the partial characterisation of the end-products of the reaction between TcO_4^- (1.6×10^{-3} mol dm^{-3}) and hydrazine (0.2 mol dm^{-3}) in a perchloric acid medium (6.0 mol dm^{-3}) containing sodium perchlorate (0.9 mol dm^{-3}). This reaction mixture slowly releases N_2 as N_2H_4 is oxidised at room temperature, turning intensely yellow after 5–6 days and displaying an ESR spectrum readily attributable to $[TcNCl_4]^-$. The yellow complex could be extracted into n-butyl acetate, retaining its ESR characteristics. On shaking this organic extract with aqueous NH_4NCS, it underwent a transformation, turning an intense inky-blue and giving a wholly different ESR spectrum, due to a new species denoted A.

A solution which is also ink-blue and displays *exactly* the same ESR spectrum and is also therefore attributed to species A, was obtained on addition of NH_4NCS to the n-butyl acetate extract from a $HClO_4$ (6.0 mol dm^{-3}) –N_2H_4–TcO_4^- reaction mixture which had been bubbled with NO during the 'fast stage' [31] of evolution of N_2. (This solution became more of a purple colour on standing for 30 min but the ESR spectrum remained unchanged.)

Figure 5 records the spectrum of species A prepared by the second method: all ten of the perpendicular features are apparent in addition to most of the parallel features. This could be computer-simulated to yield $A_\parallel$ 261×10^{-4} cm^{-1}, $g_\parallel$ 1.94, $A_\perp$ 123×10^{-4} cm^{-1}, $g_\perp$ 1.998.

Species A is *not* a $TcNX_4$ species because these invariably have $g_\parallel > 2.0$. Assignment of A to a $Tc(NO)X_5$ species strongly accords with its *g* and *A* values by comparison with the family of nitrosyltechnetium complexes shown in Fig. 2. The values are significantly different from those recorded for $[Tc(NO)(NCS)_5]^{2-}$ by Kirmse *et al.* [16] and Baldas *et al.* [21], suggesting that our product possesses fewer NCS ligands, having a formula $[Tc(NO)(NCS)_{5-x}Cl_x]^{2-}$ or $[Tc(NO)(NCS)_{5-x}Cl_y(H_2O)_{x-y}]^{x-y-2}$.

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