Electron Spin Resonance Spectrum of Tetraphenylarsonium Tetrachloro-oxochromate(V)

By **C. David Garner, Ian H. Hillier, Frank E. Mabbs,*** and **Carol Taylor**, The Chemistry Department, Manchester University, Manchester M13 9PL
Martyn F. Guest, S.R.C. Atlas Computer Laboratory, Chilton, Didcot, Berkshire OX11 0QY

The single-crystal e.s.r. parameters for $[AsPh_4][CrCl_4O]$ giving $g_{\parallel}$ 2.006 ± 0.002 and $g_{\perp}$ 1.979 ± 0.002 are reported (where $g_{\parallel}$ coincides with the Cr–O direction). Solution measurements in CH_2Cl_2 give $\bar{g}$ 1.988 ± 0.001 and $\bar{a}$ 18.1 × 10^{-4} cm^{-1}, and the addition of excess of $[NEt_4]Cl$ to these solutions results in an additional e.s.r. signal at $\bar{g}$ 1.970 ± 0.001 which is attributed to the $[CrCl_5O]^{2-}$ species. The e.s.r. parameters have been interpreted using an *ab initio* molecular-orbital approach as well as the more conventional molecular-orbital approach. The results of these two approaches are critically compared.

THE electronic structures of the d^1 mono-oxo-chromophores $[VO]^{2+}$, $[CrO]^{3+}$, and $[MoO]^{3+}$ have received considerable attention in recent years.[1-23] Except for a small number of examples in the case of vanadium, very few data are available for definitely characterised compounds of a known crystal structure. Our recent e.s.r. studies[23] of chloro-complexes of the $[MoO]^{3+}$ cation suggest that many previous solution and dilute single-crystal measurements could be of doubtful value since the species present may not be known for certain. In view of this lack of data we have undertaken a systematic study of compounds in this area and now report the single-crystal e.s.r. spectrum of $[AsPh_4][CrCl_4O]$. We also include a detailed discussion of the interpretation of the e.s.r. data in conjunction with the recently reported single-crystal polarised electronic spectrum and *ab initio* molecular-orbital (m.o.) calculations of the above compound.[22]

EXPERIMENTAL

Single crystals of $[AsPh_4][CrCl_4O]$ were prepared as described earlier.[22]

E.S.R. Spectra.—Single-crystal and solution e.s.r. spectra were obtained at room temperature on equipment and by methods described previously.[24] Single crystals were mounted on quartz rods such that spectra could be obtained in a plane containing $g_{\parallel}$ (parallel to the crystal c axis) and $g_{\perp}$ and also in a plane perpendicular to $g_{\parallel}$.† These measurements gave g 2.006 ± 0.002 and g 1.979 ± 0.002. No chromium hyperfine splittings were observed at any orientation of the crystal. The peak-to-peak width of the derivative spectrum varied from 44 G at $g_{\parallel}$ to 34 G at $g_{\perp}$ with a minimum value of 20 G at 60° from $g_{\parallel}$, whilst in the crystallographic ab plane the linewidth varied from a maximum of 34 G to a minimum of 18 G.‡ Solutions in CH_2Cl_2 gave $\bar{g}$ 1.988 and $\bar{a}$ 18.1 × 10^{-4} cm^{-1}, the width of the line due to chromium nuclei with $I = 0$ being 8 G. Addition of excess of $[NEt_4]Cl$ to the CH_2Cl_2 solutions resulted in the appearance of an additional absorption at $\bar{g}$ 1.970; by analogy with the $[MoCl_4O]^-$ system,[23] we attribute this new absorption to the formation of $[CrCl_5O]^{2-}$.

DISCUSSION

Interpretation of the E.S.R. Parameters of $[CrCl_4O]^-$.—The e.s.r. parameters obtained for $[AsPh_4][CrCl_4O]$ are in very good agreement with those reported for $[CrCl_5O]^{2-}$ by other workers.[1,2,6,18] The unambiguous characterisation of the $[CrCl_4O]^-$ ion reported here, and the fact that the addition of $[NEt_4]Cl$ to a dichloromethane solution of $[AsPh_4][CrCl_4O]$ produced a new signal at $\bar{g}$ 1.970, indicates that the compounds studied earlier, and thought to be $[CrCl_5O]^{2-}$, were in fact $[CrCl_4O]^-$.

We have used two complementary approaches to interpret the e.s.r. parameters obtained for $[CrCl_4O]^-$.

Ab initio *molecular-orbital calculation*. This is potentially the most satisfactory way of interpreting e.s.r. parameters of relatively simple species. We previously presented a calculation by the restricted Hartree–Fock method of the $^2B_2$ ground state of this ion and used[22] the m.o.s so calculated as a basis for a limited configuration-interaction calculation, including single excit-

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† Crystals of this compound have been shown to possess the tetragonal space group P_4/n, and to contain the $[CrCl_4O]^-$ unit with all the Cr–O vectors parallel to the unique crystallographic axis (A. T. McPhail, personal communication).

‡ 1 G = 10^{-4}T.

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ations from the $^2B_2$ ground state, in order to describe the excited states of $[CrCl_4O]^-$. Values for the magnetic g values were calculated using the results of perturbation theory, giving the various components of the g tensor as (1) where the summation is over all the excited states,

$$g_{ij} = 2.0023 + 4 \sum_{n \neq 0} \frac{\langle n| \sum_{N,k} (Z_N/r_{N,k}^3) l_i \cdot s_i |^2B_2\rangle \langle ^2B_2|l_j|n\rangle}{[E(^2B_2) - E_n]} \quad (1)$$

n, of the appropriate symmetry. In (1) we have written the spin–orbit Hamiltonian ($\mathscr{H}_{so}$) as in (2)

$$\mathscr{H}_{so} = \sum_N \sum_k (Z_N/r_{N,k}^3) l \cdot s \quad (2)$$

where the summation is over all the nuclei, N, with effective nuclear charge Z_N. The charges were estimated using Slater's rules together with the calculated atomic populations obtained from a Mulliken analysis of the $^2B_2$ ground state.[22] Thus, the atomic configurations were found to be approximately Cr $3d^3$ and Cl $3s^23p^6$ which gave $Z_{Cr} = 5.3$ and $Z_{Cl} = 5.75$.

We first consider the calculation of $g_\perp$, which is determined by the admixture of ^2E excited states into the $^2B_2$ ground state [equation (1)]. The lowest ^2E excited state is predicted [22] to be predominantly due to the orbital transition $3b_2 \rightarrow 13e$ ($d \rightarrow d$) and is calculated to be 9 900 cm^{-1} above the ground state. We have correlated this state with the first transition observed for $[CrCl_4O]^-$ at 13 100 cm^{-1}. If we use the virtual-orbital approximation to represent the ^2E state, then we may write (3) where the m.o.s $3b_2$ and $13e$ correspond

$$g_\perp = 2.0023 + \frac{2\langle 13e|\sum_N Z_N/r_N^3) l_x|3b_2\rangle\langle 3b_2|l_x|13e\rangle}{[E(^2B_2) - E(^2E)]} \quad (3)$$

to b_2^* and e^* in the empirical approach discussed later. The integrals in equation (3) were evaluated exactly in terms of the $13e$ and $3b_2$ m.o.s obtained from the *ab initio* calculation on the $^2B_2$ ground state. The integrals involving the atomic basis functions and the operators $1/r^3$ and l were evaluated in terms of the corresponding dipole-moment and field-gradient integrals, to give $\langle 13e|l_x/r_{Cr}^3|3b_2\rangle = -3.097i$ a.u. and $\langle 13e|l_x|3b_2\rangle = -0.865i$ a.u. These values, together with the calculated excitation energy (9 900 cm^{-1}), lead to $g_\perp$ 1.968. However, if the experimental excitation energy of 13 100 cm^{-1} is used we obtain $g_\perp$ 1.977 in excellent agreement with the observed value. It should be noted that the angular-momentum integral is reduced from the value of $-i$ due to the covalency in both the $3b_2$ and $13e$ m.o.s which are calculated to have a metal $3d$ character of 95 and 80%, respectively.

Several other ^2E excited states are calculated to be reasonably close in energy to this first ^2E state. These arise due to the promotion of an electron from a doubly occupied m.o. (d.o.m.o.) to a virtual m.o. (v.m.o.) and these transitions have been correlated with other bands in the absorption spectrum of $[CrCl_4O]^-$. However, as Glarum [25] has pointed out, such excitations do not contribute to g values calculated from equation (1). The next ^2E state which could contribute involves the excitation $9e \rightarrow 3b_2$, where an electron is promoted from d.o.m.o. $9e$ to singly occupied m.o. (s.o.m.o.) $3b_2$ (corresponding to $e \rightarrow b_2^*$ in the empirical approach). We calculate the transition energy to this state to be greater than 50 000 cm^{-1}. Such a high transition energy coupled with the small degree of d-orbital character in the $9e$ m.o. (16%) leads to a small increase in $g_\perp$ of *ca.* 0.001 resulting from the coupling of this ^2E state with the ground state. We can neglect such a small change and thus $g_\perp$ may be satisfactorily interpreted solely in terms of coupling the first ^2E excited state.

The interpretation of $g_\parallel$ is rather more complicated than that of $g_\perp$. The measured value of the former, 2.006, being greater than the spin-free value, suggests that it is influenced by a $^2B_1$ excited state resulting from electron promotion from a d.o.m.o. to the s.o.m.o. $3b_2$. Such a transition is $6b_1 \rightarrow 3b_2$ (corresponding to $b_1 \rightarrow b_2^*$ in the empirical scheme); the $6b_1$ m.o. is calculated to have 38% d-orbital character. We calculate that this $^2B_1$ excited state will yield an increase in $g_\parallel$ of $926/\Delta E(6b_1 \rightarrow 3b_2)$ from the spin-free value [where $\Delta E(6b_1 \rightarrow 3b_2)$ is in cm^{-1}]. The other $^2B_1$ state which is expected to be of importance in the interpretation of $g_\parallel$ involves the excitation from the s.o.m.o. ($3b_2$) to the v.m.o. ($8b_1$). In the ground state of the compound the latter m.o. is calculated to have 58% d-orbital character, and the use of the form of the $3b_2$ and $8b_1$ m.o.s so calculated from equation (1) leads to an estimated decrease in $g_\parallel$ of $734/\Delta E(3b_2 \rightarrow 8b_1)$ [where $\Delta E(3b_2 \rightarrow 8b_1)$ is in cm^{-1}].

The net result of this consideration of these two $^2B_1$ excited states gives $g_\parallel = 2.0023 - [734/\Delta E(3b_2 \rightarrow 8b_1)] + [926/\Delta E(6b_1 \rightarrow 3b_2)]$. Previous workers have assigned the absorption observed at 18 100 cm^{-1} in the spectrum of $[CrCl_4O]^-$ to the excitation $3b_2 \rightarrow 8b_1$. The results of the polarised single-crystal spectral study [22] show that this assignment is probably incorrect. Furthermore, the experimental determination of the $3b_2 \rightarrow 8b_1$ transition appears to be almost impossible in this system since [22] it is expected to be extremely weak and to be obscured by intense charge-transfer transitions. No observations of the excitation $6b_1 \rightarrow 3b_2$ have been reported. This lack of experimental data thus dictates that the computational estimates of these excitation energies have to be used in order to estimate $g_\parallel$. We calculate the values of the $3b_2 \rightarrow 8b_1$ and the $6b_1 \rightarrow 3b_2$ excitation energies to be 22 400 and 42 000 cm^{-1}, respectively.[22] These values lead to a value of $g_\parallel$ of 1.992 which is in rather poor agreement with the experimental value. However, a comparison [22] of the experimental and computed transition energies suggested that our configuration-interaction calculations underestimate the energies of the d–d transitions and overestimate the energies of the charge-transfer transitions by *ca.* 30% in each case. The $3b_2 \rightarrow 8b_1$ excitation is predominantly d–d in character whereas $6b_1 \rightarrow 3b_2$ is predominantly a

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[25] S. H. Glarum, *J. Chem. Phys.*, 1963, **39**, 3141.

charge-transfer excitation. The suggested modifications in their computed energies lead to an estimate of $g_{\parallel}$ of 2.007, in good agreement with the experimental value.

An empirical approach. Following the procedure outlined earlier,[1,26] the m.o.s have been constructed for $[CrCl_4O]^-$ assuming a square-pyramidal geometry and using metal d and ligand p orbitals. The axis system due to Ballhausen[27] leads to expressions (4)—(8) and (9)—(13) for the metal–ligand antibonding and bonding orbitals respectively. Using these molecular orbitals,

$$a_1^* = N_1'[d_{z^2} - \alpha_3 z_3 + \alpha(z_1 + z_2 + z_4 + z_5)] \quad (4)$$

$$b_1^* = N_2'[d_{x^2-y^2} + \beta(z_2 + z_5 - z_1 - z_4)] \quad (5)$$

$$b_2^* = N_3'[d_{xy} - \delta(x_1 + y_2 + x_5 + y_4)] \quad (6)$$

$$e_1^* = N_4'[d_{xz} - \gamma(y_1 + x_4) - \gamma_3 x_3] \quad (7)$$

$$e_2^* = N_5'[d_{yz} - \gamma(x_2 + y_5) - \gamma_3 y_3] \quad (8)$$

$$a_1 = N_1[(\alpha_3 + 4\alpha)d_{z^2} + az_3 - b(z_1 + z_2 + z_4 + z_5)] \quad (9)$$

$$b_1 = N_2[4\beta d_{x^2-y^2} + z_1 - z_2 + z_4 - z_5] \quad (10)$$

$$b_2 = N_3[4\delta d_{xy} + x_1 + y_2 + x_5 + y_4] \quad (11)$$

$$e_1 = N_4[(\gamma_3 + 2\gamma)d_{xz} + cx_3 + d(y_1 + x_4)] \quad (12)$$

$$e = N_5[(\gamma_3 + 2\gamma)d_{yz} + cy_3 + d(y_5 + x_2)] \quad (13)$$

and allowing for spin–orbit coupling between the $(a_1)^2(b_1)^2(e)^4(b_2)^2(b_2^*)^1$ ground state and various excited states obtained from this by single-electron excitation, with the approximation that terms in $(1/\Delta E)^2$ (where ΔE is the appropriate excitation energy) and overlap terms can be ignored, we have equations (14)—(22),

$$g_{\parallel} = 2.0023 - N_2'N_3'A(8 - 16\delta\beta) + 16(\beta + \delta)N_3'N_2B \quad (14)$$

$$g_{\perp} = 2.0023 - N_3'N_4'D(4 + 8\gamma\delta) + 4N_3'N_4(\gamma_3 + 2\gamma)F \quad (15)$$

$$\frac{A_{\parallel}}{P} = -\frac{4}{7}(N_3')^2 - K(N_3')^2 + (g_{\parallel} - 2.0023 - 16\delta\beta AN_2'N_3') - \frac{3}{7}[2.0023 - g_{\perp} - 8\gamma\delta N_3'N_4'D - 2FN_3'N_4(\gamma_3 + 2\gamma)] \quad (16)$$

$$\frac{A_{\perp}}{P} = \frac{2}{7}(N_3')^2 - K(N_3')^2 - \frac{11}{14}(2.0023 - g_{\perp}) + 32N_3'N_4'D\gamma\delta + \frac{3}{14}\left[\frac{3}{2}FN_3'N_4(\gamma_3 + 2\gamma) - N_3'N_4'D8\gamma\delta\right] \quad (17)$$

$$A = \frac{N_2'N_3'}{E(b_2^* \rightarrow b_1^*)}(\xi_M - \xi_{Cl}2\beta\delta) \quad (18)$$

$$B = \frac{N_2N_3'}{E(b_1 \rightarrow b_2^*)}(4\beta\xi_M + \xi_{Cl}2\delta) \quad (19)$$

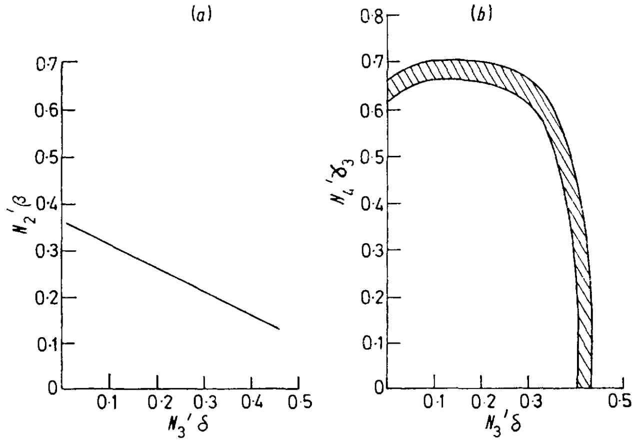
$$D = \frac{N_3'N_4'}{2E(b_2^* \rightarrow e^*)}(\xi_M + \xi_{Cl}2\delta\gamma) \quad (20)$$

$$F = \frac{N_3'N_4}{2E(e \rightarrow b_2^*)}[(\gamma_3 + 2\gamma)\xi_M - \xi_{Cl}2\delta d] \quad (21)$$

$$P = 2g_N\beta\beta_N\langle r^{-3}\rangle \quad (22)$$

where K is the Fermi isotropic-interaction constant and ξ_M and ξ_{Cl} are the single-electron spin–orbit coupling constants for the metal d and chlorine $3p$ orbitals respectively.

The expressions for the four e.s.r. parameters thus involve the eight parameters β, δ, γ, γ_3, ξ_M, ξ_{Cl}, P, and K as well as the four excitation energies which correspond to those discussed in the *ab initio* treatment above. The determination of the relative magnitudes of the m.o. coefficients β, δ, γ, and γ_3 from e.s.r. data has occupied a number of authors[1,2,9,17-21] and a variety of approximations have been adopted, some of which have been assessed by Van Kemenade.[19] The treatment described above differs from those considered previously in the inclusion of π bonding between the metal d_{xz}, d_{yz} orbitals, and the chlorine p_{π} orbitals and also the inclusion of the F term. However, the *ab initio* calculations indicate that in the case of $[CrCl_4O]^-$ this latter term makes a very small contribution because of the large value of $E(e \rightarrow b_2^*)$ and the relatively small metal-orbital content of the e orbitals.



Plots of the fits of g_i [= g_i (expt.) − g_i (calc.)] from the empirical molecular orbital approach: (*a*) $g_{\parallel}$; (*b*) $g_{\perp}$. For ξ_{Cr} = 275 cm^{-1}, ξ_{Cl} = 587 cm^{-1}, and $N_4'\gamma$ = 0.15; $E(b_2^* \rightarrow b_1^*)$ = 29 600, $E(b_1 \rightarrow b_2^*)$ = 31 500, and $E(b_2^* \rightarrow e^*)$ = 13 100 cm^{-1}. The shaded area represents the range of parameters which fit $g_{\perp}$ to within ±0.002.

The difficulties in assigning unambiguous values to the various excitation energies required in (18)—(21) have been discussed in the previous section. However, even if these energies can be found, the determination of unique values for the m.o. parameters does not readily follow from this empirical treatment. This is illustrated in the Figure, where the m.o. parameters required to account for the experimental g values are shown for 'realistic' values of ξ_{Cr}, ξ_{Cl}, and the transition energies. Thus the interpretation of $g_{\parallel}$ involves β and δ, whilst that of $g_{\perp}$ involves δ, γ_3, and γ. This lack of uniqueness of fit has been resolved in the present case by giving γ arbitrary fixed values (γ was chosen because the *ab initio* calculations indicated that it was small) and finding an approximate value of N_3' and

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[26] B. R. McGarvey, *Transition Metal Chem.*, 1966, **3**, 89.

[27] C. J. Ballhausen, 'Introduction to Ligand Field Theory,' McGraw-Hill, 1962.

hence δ from the hyperfine splitting constants as indicated by Kon and Sharpless.[1] This approximation involves ignoring terms in A, D, and F in equations (16) and (17) but subsequent estimations of the omitted terms show them to be *ca.* 10^{-3} times the major terms in the expressions. The value of δ obtained by this approach depends critically on the formal charge state of chromium assumed in the complex, since this determines the value of P employed. The same problem arises in choosing the value of ξ_{Cr}.

Assuming that the chromium hyperfine splitting constants previously reported for $[CrCl_5O]^{2-}$ are relevant to $[CrCl_4O]^-$, the values of the m.o. coefficients obtained by the above treatment are summarised in the Table. These are compared with the values from the *ab initio* treatment and also those previously reported by other workers. The percentage chromium d-orbital character in the m.o.s shows a marked dependence on the formal charge assumed for the chromium ion. Also the d orbital character in the metal e^* m.o. shows a significant variation as the chlorine p_π contribution to e^* is varied in the range 0—5%. (The effect of higher percentages was not investigated.) Values of the m.o. parameter close to those from the *ab initio* calculation were obtained using a formal charge on the chromium of +1.5. This value is gratifyingly close to the +1.65 obtained from the *ab initio* treatment.

This agreement between the two approaches calls for some further comment. Assuming that we have been able to choose the parameters P and ξ_{Cr} correctly, the estimation of the percentage metal d-orbital character in the b_2^* and e^* orbitals depends on the experimental $A_{\parallel}$, $A_{\perp}$, $g_{\parallel}$, and $g_{\perp}$ values and on the assignment of $E(b_2^* \rightarrow e^*)$. This latter assignment seems to be reasonably certain from the experimental data. The close agreement in these instances suggests that the assumption of a regular square-pyramidal geometry and the neglect of overlap contributions to the e.s.r. parameters are not serious in the present case. The estimation of the percentage metal d-orbital character in the b_1^* orbital depends on the experimental value of $g_{\parallel}$ and on the transition energies $E(b_2^* \rightarrow b_1^*)$ and $E(b_1 \rightarrow b_2^*)$. Since we have not been able to determine these transition energies experimentally, we have used the scaled values from the *ab initio* calculations as given earlier. Thus it is not too surprising that we obtain good agreement with the *ab initio* calculation for this metal d-orbital coefficient.

Assumed charge on chromium in complex	$\frac{-10^4P}{cm^{-1}}$	$\frac{\xi^{b}}{cm^{-1}}$	Assumed % Cl (p_π) in e^*	K	Calculated % of metal character in			Ref.
					b_2^*	e^*	b_1^*	
ab initio					95	80	58	22
3	39.7 [a]	275	5	0.575	78	50	77	*c*
2	34.6 [a]	230	5	0.577	90	62	68	*c*
1.5	32.0 [a]	205	5	0.583	96	70	65	*c*
1.5	32.0 [a]	205	0	0.583	96	77	62	*c*
3	39.7 [a]	275	0	0.60	78.5	91.8	35.1	18
5	35.5	383	0	0.60	86.8	48.9	76.4	1
4	35.5	325	0	0.60	86.8	57.6	77.4	1
3	35.5	275	0	0.60	86.8	68.1	77.5	1
2	35.5	230	0	0.60	86.8	81.4	81.8	1
1	35.5	190	0	0.60	86.8	98.5	84.6	1

Excitation energies used for $E(b_2^* \rightarrow b_1^*)$ and $E(b_1 \rightarrow b_2^*)$ were 29 600 and 31 500 cm^{-1} obtained by scaling the *ab initio* calculation (see text); K is the Fermi isotropic interaction constant.

[a] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51. [b] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441. [c] This work.

The very different values of the m.o. coefficients obtained by previous workers, even when the same formal charge on the chromium ion was assumed, arises primarily from the previous erroneous interpretation of the electronic-absorption spectrum, namely that the second band in the absorption spectrum at 18 100 cm^{-1} is due to the $b_2^* \rightarrow b_1^*$ transition.

[6/823 *Received, 28th April*, 1976]