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Preliminary communication

EPR spectra of chromium(IV) in tetrakis-alkyl chromium compounds

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INTRODUCTION

Bowen and Tennent[1] and Kruse[2] have described the preparation and properties of a novel series of tetrakis-alkyl chromium(IV) and tris-alkyl chromium(III) compounds. In the course of efforts to characterize these compounds, we have found electron paramagnetic resonance (EPR) to be very useful for determining the oxidation state of alkylmetal compounds, and have obtained EPR spectra of both the CrR_4 and CrR_3 compounds. The fact that the d^2 chromium(IV) compounds exhibit a well-defined EPR spectrum at +25° using X-band frequencies is novel as well as useful, since zero-field splitting effects usually make the observation of the EPR of d^2 ions very difficult. In fact, to our knowledge, the only previous reports of an EPR signal due to a chromium(IV) compound were that of Hoskins and Soffer[3] who detected the "forbidden" $\Delta m = 2$ transition of Cr^{IV} in an Al_2O_3 lattice, and that of Alyea *et al.*[4] who reported the only previous EPR spectrum of a discrete Cr^{IV} compound, $Cr(O\text{-}t\text{-}Bu)_4$. The spectrum of the latter compound was observed only at 10 K, however, due to rapid relaxation at higher temperatures.

RESULTS AND DISCUSSION

We have recorded the EPR spectra of a number of compounds with the general formula CrR_4, at both +25° and −196°. In general, the room temperature spectrum of these compounds consists of a single intense mid-field (H_0 near 3270 gauss) peak, the area of which is consistent with a d^2 Cr^{IV} species based on calibration with a diphenylpicrylhydrazyl standard of known concentration. At −196° a second weak absorption peak corresponding to the $\Delta m = 2$ transition between non-adjacent levels is observed in the $H = 1500$ to 1650 gauss region, in addition to the much stronger mid-field signal. A typical

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CrR_4 spectrum at −196°, where R = $-CH_2-C(CH_3)_3$ is shown in Fig. 1. The spectral data for several of the compounds studied in our work are summarized in Table 1.

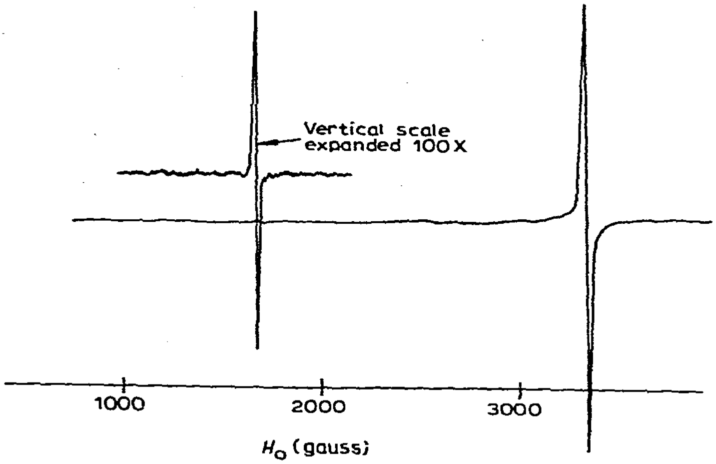

Fig. 1. EPR spectrum of 2.7 × 10^{-3} *M* tetraneopentylchromium in heptane at −196°.

TABLE 1

EPR SPECTRA OF CrR_4 COMPOUNDS AT −196°C

R	*Solvent*	*Mid-field transition*		*Low-field transition*	
		H^a	ΔH^b	H^c	ΔH^b
$CH_2CH_2CH_2CH_3$	Heptane	3270	30	1618	27
$C(CH_3)_3$	Heptane	3282	25	1630	17
$CH_2C(CH_3)_3$	Heptane	3274	47	1611	48
norbornyl	Benzene	3282	64	1627	14
$CH_2C(C_2H_5)_3$	Pentane	3270	550	1535	50
$CH_2C(CH_3)_2(C_6H_5)$	Pentane	3280	680	1580	70

[a] Center of resonance in gauss. H_0 for diphenylpicrylhydrazyl = 3255 gauss.
[b] Peak-to-peak linewidth in gauss.
[c] Center of low-field resonance, in gauss. Accuracy unknown due to lack of low-field calibration of magnet sweep.

In general, the EPR spectra of d^2 ions can be interpreted in terms of the spin Hamiltonian

$$H = \beta H g \cdot S + D(S_z^2 - 2/3) + E(S_x^2 - S_y^2)$$

which is similar to that used for organic triplets except that it does not contain terms accounting for nuclear spin—electron spin interaction[5]. The EPR of randomly oriented triplet molecules in frozen solution has been treated by a number of workers[6]. In general, the transitions between adjacent levels in randomly oriented systems for which D and E are not zero lead to a maximum of three pairs of lines separated by $2D, D + 3E$, and $D - 3E$. All three pairs are centered on the field corresponding to the g-value of the triplet: Most of the CrR_4 compounds studied in this work exhibited a narrow single mid-field line at −196°, with $\Delta H = 50$ gauss or less, so that D and E for these compounds must be very small (for $2D < 50$ gauss, for example, $d < 0.003$ cm^{-1}), and their ligand field must be very nearly tetrahedral. This would lead to a large separation between the e and t_2 levels as in the tetrahedral $FeO_4{}^{2-}$ ion[7]. In several compounds studied, however, the mid-field line was significantly broadened, as in the last two examples in Table 1. This may indicate that the large R groups in these cases required distortion of the tetrahedral symmetry of the ligand field in the frozen solution at −196° which is also consistent with the observation of the transition between non-adjacent levels at a lower field for these compounds. The linewidth of the CrR_4 EPR peaks at +25° was found to be insensitive to changes in the solution concentration over the range 0.01 to 0.0001 M.

The CrR_3 compounds studied to date give characteristic Cr^{III} EPR spectra at −196°, such as that shown for the case where R is 4-camphyl, in Fig. 2. These are very similar to the spectra shown by Hempel *et al.*[8] for polycrystalline chromium(III) compounds, and may be analyzed for the D and E values by the methods given by those authors.

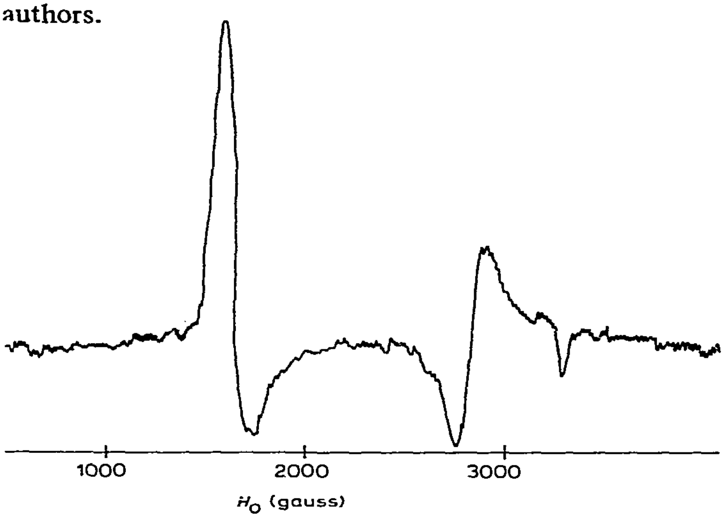

Fig. 2. EPR spectrum of tri-4-camphylchromium in pentane at −196°.

EXPERIMENTAL

Spectra were recorded on a Varian V-4500 EPR spectrometer with 100 kHz. modulation and a Fieldial control using the V-4531 general purpose EPR cavity.

The preparation of the compounds studied has been described by Kruse[2].

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Note added in proof: During the preparation of this article, the EPR spectrum of a similar Cr^{IV} compound, $Cr(CH_2SiMe_3)_4$ was reported by W. Mowat et al. (*J. Chem. Soc. (Dalton)*, (1972) 533).