

The Molecular Structure of Tetrakis(neopentyl)chromium, $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$, Determined by Gas-Phase Electron Diffraction. *Ab Initio* Molecular Orbital Calculations on CrMe_4 and CrF_4

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By introducing a bulky neopentyl ligand, homoleptic monomeric alkyls have been isolated for several transition elements. The gas-phase molecular structure of monomeric $\text{Mn}(\text{CH}_2\text{CMe}_3)_2$ has been published.¹ The gas-phase structures of $\text{Cr}(\text{O}^i\text{Bu})_4$,² and CrF_4 ,³ pseudo-isoelectronic with $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$, are also known. Tetrakis(neopentyl)chromium is sufficiently thermally stable for a gas-phase electron diffraction (GED) investigation. Although oxidation state IV is quite rare for chromium, this compound, along with other alkyls, amides and alkoxides of chromium(IV), is quite stable towards attack by water, alcohols, amines and phosphines.⁴

Electron spin resonance spectra,⁴ electronic absorption spectra⁴ and the photoelectron spectra⁵ of $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$ are all consistent with a molecular model with a tetrahedral CrC_4 core and an electronic $^3A_2(e^2)$ ground state.

Information concerning the synthesis of the compound, the GED experiments, the data reduction and the *ab initio* calculations is given in the Appendix.

Model choice and refinements

Refinements were carried out on models with S_4 , D_{2d} , C_2 and C_1 symmetry. Of these only the S_4 model, shown in Fig. 1, could be brought into satisfactory agreement with the experimental data, giving a final value of R of 0.045.[†] Even though they require the refinement of a greater number of independent parameters, the other models yielded R factors ranging from 0.056 to 0.068.

The S_4 model was characterized by three independent bond distances, $r(\text{Cr}-\text{C})$, $r(\text{C}-\text{C})$ and $r(\text{C}-\text{H})$, and by four valence angles, $\angle\text{C}'-\text{Cr}-\text{C}$, $\angle\text{C}-\text{C}-\text{C}^*$, $\angle\text{C}-\text{C}^*-\text{C}1$ and $\angle\text{C}^*-\text{C}1-\text{H}$. The methylene protons were arbitrarily fixed in a plane bisecting $\angle\text{Cr}-\text{C}-\text{C}^*$ with $\angle\text{H}-\text{C}-\text{H} = 109.47^\circ$. Initial refinements were carried out with $\angle\text{C}'-\text{Cr}-\text{C}$ fixed

at 109.47° . Subsequent refinements of this parameter did not improve the fit: it converged to ca. $110.7(2.2)^\circ$ independently of the starting value. All refinements with this angle fixed at values smaller or greater than tetrahedral gave an increased R factor. In the final refinements $\angle\text{C}'-\text{Cr}-\text{C}$ was again fixed at 109.47° . Refinements were also carried out on models in which the C^*Me_3 fragments were allowed to tilt in the direction of increasing $\text{C}=\text{C}2$ and $\text{C}=\text{C}3$ distances. (In the final refinements the tilt angle θ was fixed at 1.5° .) The remaining two independent parameters are torsional angles: $\varphi(\text{C}'-\text{Cr}-\text{C}^*)$ and $\varphi(\text{Cr}-\text{C}-\text{C}^*-\text{C}1)$.

Results and discussion

An experimental radial distribution curve and the corresponding curve calculated for the best model are compared in Fig. 2. Selected structure parameters and vibrational amplitudes are listed in Table 1. Least-squares standard

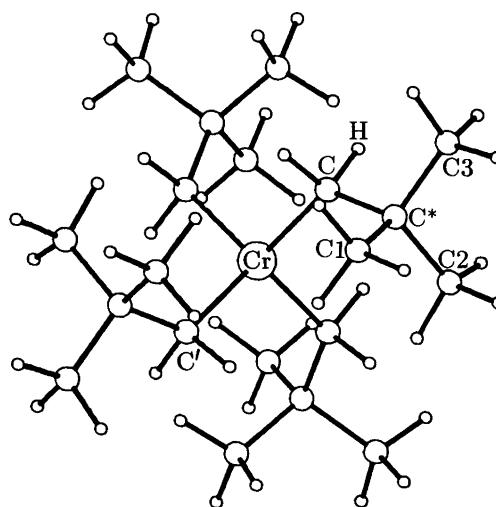


Fig. 1. Molecular model of $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$. Symmetry S_4 .

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[†] $R = (\sum w(I_{\text{obs}} - I_{\text{calc}})^2 / \sum w I_{\text{obs}}^2)^{1/2}$.

errors have been multiplied by a factor of three to compensate for data correlation and the assumptions made when defining the model. Of the correlation coefficients, only $r(\text{Cr}-\text{C})/r(\text{C}^*=\text{H})$ of 77% and $\angle\text{Cr}-\text{C}-\text{C}^*/\angle\text{C}-\text{C}^*-\text{C1}$ of -71% are of concern.

The Cr-C bond distance in $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$ is in reasonable agreement with the bond distances found by X-ray crystallography in two other Cr(IV) tetraalkyls, the mean $r(\text{Cr}-\text{C})$ in $\text{Cr}(\text{CH}_2\text{CMe}_2\text{Ph})_4$ is 205(3) pm,⁶ and the two crystallographically independent Cr-C bond distances in

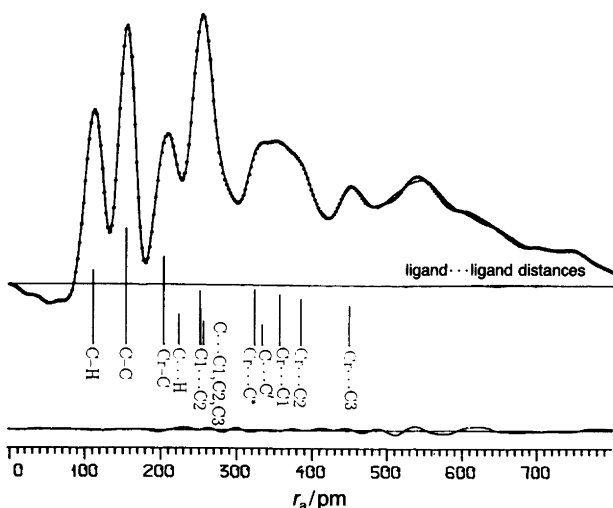


Fig. 2. Radial distribution curves, experimental (dotted line) and theoretical (full line). below: difference curve. Artificial damping constant 30 pm².

Table 1. Selected structure parameters and vibrational amplitudes for $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$ determined by GED.^a

Bond distances:	r_a/pm	l/pm	
Cr-C	203.8(8)	6.9(7)	
C-C	154.5(3)	5.2(3)	
C-H	110.9(4)	7.6(4)	
Non-bonded distances:			
Cr...C*	323(1)	9.8(11)	
Cr...C1	357(2)	18(3)	
Cr...C2	385(2)	13(1) ^b	
Cr...C3	449(1)	14(1) ^b	
C1...C2	250(2)	8.1(4) ^c	
C...C1 (average)	253(2)	8.1(4) ^c	
C*...H	223(1)	11(2)	
C'...C	333(1)	21(5)	
Bond angles (in °):		Torsional angles (in °):	
$\angle\text{Cr}-\text{C}-\text{C}^*$	128.0(8)	$\varphi(\text{C}'-\text{Cr}-\text{C}-\text{C}^*)$	56(2)
$\angle\text{C}-\text{C}^*-\text{C1}$	110.7(8)	$\varphi(\text{Cr}-\text{C}-\text{C}^*-\text{C3})$	16(2)
$\angle\text{C}^*-\text{C1}-\text{H}$	113.3(7)		
$\angle\text{C}'-\text{Cr}-\text{C}^*$	[109.47] ^d		
Tilt	[1.5] ^d		

^aEstimated standard deviations are given in parentheses in units of the last digit. ^bRefined with equal shift. ^cRefined with equal shift. ^dSee comment in text.

$\text{Cr}(\text{cyclo-C}_6\text{H}_{11})_4$ are 201.0(4) and 200.9(4) pm, respectively.⁷ Other alkyls with chromium in lower oxidation states appear to have somewhat longer Cr-C bonds: the calculated (MCPF) Cr-C distance in CrMe_2 is 207 pm,⁸ and in $\text{Cr}(\text{II})(\text{CH}_2\text{CMe}_3)_2\text{dippe}$ (a tetrahedrally distorted square-planar complex) Cr-C = 214.9(8) pm.⁹ The $\angle\text{Cr}-\text{C}-\text{C}^*$ angle is significantly larger than the corresponding angle in $\text{Mn}(\text{CH}_2\text{CMe}_3)_2$, 120(1)°,¹ probably owing to additional steric strain introduced by both a shorter M-C bond and a larger number of bulky ligands.

We find no evidence for distortion from a tetrahedral CrC_4 core. Similar negative conclusions have been reached in spectroscopic studies.^{4,5} The crystal structures of $\text{Cr}(\text{CH}_2\text{CMe}_2\text{Ph})_4$ and $\text{Cr}(\text{cyclo-C}_6\text{H}_{11})_4$ indicate slightly flattened tetrahedral coordination geometries: the mean angles $\angle\text{C}'\text{CrC}$ are 113° (Ref. 6) and 114° (Ref. 7), respectively. If these compounds have electronic ground states of 3A_2 symmetry, the reason for the distortion must be sought in steric interaction between the ligands or between molecules.

Gas electron diffraction studies of $\text{Cr}(\text{OCMe}_3)_4$ ² and CrF_4 ³ similarly failed to give evidence for distortion from tetrahedral coordination geometry. The bond distances to Cr are, however, much shorter than in the alkyls; Cr-O = 175.1(7) pm and Cr-F = 170.6(2) pm. The shortening may be due to the smaller covalent radii of O and F, to electronegativity difference effects, and possibly to dative Cr-O and Cr-F π -bonding.

In order to elucidate possible π -bonding effects we carried out *ab initio* MO calculations on CrMe_4 and CrF_4 . Total energies, optimized geometries, orbital energies and Mulliken parameters are listed in Table 2. The optimized bond distances are in good agreement with experimental values. The $\epsilon(3d)$ and Cr-C ionization potentials determined from the photoelectron spectrum of $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$ are 7.25 and 8.69 eV, respectively,⁵ much smaller than estimated from the orbital energies and Koopmans' theorem; relaxation energies are apparently not negligible. The effective atomic charges on Cr are +1.679 in CrMe_4 and +1.835 in CrF_4 .

π -Interactions in tetrahedral systems are complicated to analyse. The ligand π -orbitals (transforming as t_1+t_2+e) may interact with both the $d(e+t_2)$ and p_π orbitals on the metal. The population of each of the $d(e)$ orbitals, usually considered as the d_π orbitals, is indeed somewhat higher in CrF_4 than in CrMe_4 , but the population of the (σ -antibonding) $d(t_2)$ is higher in CrMe_4 than in CrF_4 . Our conclusion must again be put in the negative: the calculations do not provide clear-cut evidence for significant π -bonding in CrF_4 .

Appendix: Experiment, data processing and calculations

$\text{Cr}(\text{CH}_2\text{CMe}_3)_4$ was prepared from $\text{Me}_3\text{CCH}_2\text{Li}$ and $\text{CrCl}_3(\text{thf})_3$ as previously described.⁴ The compound was purified by crystallization from pentane as purple-red

Table 2. *Ab initio* restricted Hartree–Fock calculations on Cr(CH₃)₄ and CrF₄, state ³A₂. Optimized geometry, Mulliken population parameters, orbital energies and total energies.

	Cr(CH ₃) ₄	CrF ₄
r_{\min}/pm	200	171
r_{exp}/pm	203.8 ^a	170.6
Atomic charges:		
Cr	+1.679	+1.853
C	-1.015	
F		-0.462
H	+0.196	
Orbital populations:		
$d(t_2)$	0.613	0.415
$d(e)$	1.002	1.138
Orbital energies/eV:		
$a_1(\text{Cr-ligand bond})$	-11.67	-19.59
$t_2(\text{Cr-ligand bond})$	-11.08	-19.25
$e(3d \text{ orbital})$	-19.6	-22.3
Total energy/a.u.	-1201.5462	-1441.1916

^aFrom GED data on Cr(CH₂CMe₃)₄, present work.

needles, then sublimed at 40–50°C in vacuum, m.p. 109–111°C. The electron ionization mass spectrum gave a molecular ion centred around 336 amu.

The GED data were recorded on a Balzers Eldiograph KDG-2.^{10,11} The nozzle and reservoir temperatures were about 130°C. The electronic wavelength has been calibrated against the C–C bond distance in gaseous benzene ($r_a = 139.75$ pm). Two sets of data were recorded, four plates with a nozzle-to-plate distance of 50 cm, and four plates with a distance of 25 cm. The s -limits used in the final

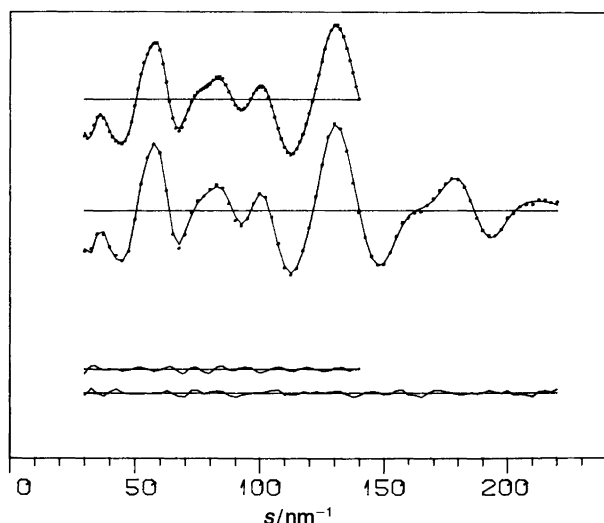


Fig. 3. Intensity curves, experimental (dotted line) and theoretical (full line). Below: difference curve.

refinements were $s = 30.0\text{--}140.0 \text{ nm}^{-1}$ with $\Delta s = 1.25 \text{ nm}^{-1}$ (50 cm) and $s = 30.0\text{--}220.0 \text{ nm}^{-1}$ with $\Delta s = 2.50 \text{ nm}^{-1}$ (25 cm). After photometry on a Joyce–Loebl densitometer the data were processed by standard procedures.¹² The backgrounds were by drawn computer, and finally the intensity curves were averaged within each set of data. Complex atomic scattering factors $f'(s)$ were taken from Ref. 13. The intensity curves for the best model are shown in Fig. 3.

Ab initio open-shell restricted Hartree–Fock calculations have been carried out on CrF₄ and CrMe₄ using the program DISCO.¹⁴ For both molecules we have chosen the state ³A₂ in the point group T_d . The Gaussian-type basis on chromium was [15, 9, 7], contracted to <12, 9, 5> taken from Ref. 15; a diffuse p-function with exponent 0.17 was added. The basis sets on carbon and fluorine were [9, 5], contracted to <4, 3> from Ref. 16, and on hydrogen [3], contracted to <2> from Ref. 17. The geometry was fixed with $\angle\text{CrC–H}$ at 109.5° and the C–H bond distance at 109 pm. The Cr–C and Cr–F optimal bond distances are obtained from interpolation using four points.

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References

- Andersen, R. A., Haaland, A., Rypdal, K. and Volden, H. V. *J. Chem. Soc., Chem. Commun.* (1985) 1807.
- Thaler, E. G., Rypdal, K., Haaland, A. and Caulton, K. G. *Inorg. Chem.* 28 (1989) 2431.
- Hedberg, L., Hedberg, K., Gard, G. L. and Udeaja, J. O. *Acta Chem. Scand., Ser. A* 25 (1988) 318.
- Mowat, W., Shortland, A. J., Hill, N. J. and Wilkinson, G. J. *J. Chem. Soc., Dalton Trans.* (1973) 770.
- Evans, S., Green, J. C. and Jackson, S. E. *J. Chem. Soc., Faraday Trans. 2*, 69 (1973) 191.
- Gramlich, V. and Pfefferkorn, K. *J. Organomet. Chem.* 61 (1973) 247.
- Stavropoulos, P., Savage, P. D., Tooze, R. P., Wilkinson, G., Hussain, B., Motevalli, M. and Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* (1987) 557.
- Rosi, M., Bauschlicher, C. W., Jr., Langhoff, S. R. and Patridge, H. J. *Phys. Chem.* 94 (1990) 8656.
- Hermes, A. R., Morris, R. J. and Girolami, G. S. *Organometallics* 7 (1988) 2372.
- Zeil, W., Haase, J. and Wegmann, L. *Instrumentenk. d.* 74 (1966) 84.
- Bastiansen, O., Graber, R. and Wegmann, L. *Balzers High Vacuum Rep.* 25 (1969) 1.
- Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
- (a) Schafer, L., Yates, A. C., Bonham, R. A. *J. Chem. Phys.* 55 (1971) 3055; (b) *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
- Almlöf, J., Faegri, K., Jr. and Korsell, K. *J. Comput. Chem.* 3 (1982) 385.
- Faegri, K., Jr. and Speis, H. J. *J. Chem. Phys.* 86 (1987) 7035.
- Dunning, T. H. *J. Chem. Phys.* 53 (1970) 2823.
- Huzinaga, S. *J. Chem. Phys.* 42 (1965) 1293.

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