spectral and redox properties of the $XW_{12}O_{40}$-type heteropolytungstates[17,18] appear ideal for oxidative quenching. We are also studying the photochemical properties of the related $Mo_6Br_{14}^{2-}$ and $W_6Cl_{14}^{2-}$ ions.

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(17) Varga, G. M., Jr.; Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1970**, *9*, 662-667.

(18) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547-2553.

Eigenfunctions of Open-Shell Molecules: Experimental Spin Densities in CrF_6^{3-} and $CoCl_4^{2-}$

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Diffraction of X-rays, electrons, and neutrons by crystals offers the only direct relationship between observations (Bragg intensities) and the wave function sampling, for example, Fourier components of the electron density or, in the case of polarized neutron scattering, the magnetization density. The magnetization density is due to both the intrinsic magnetic moment of electrons (spin) and the magnetic moment generated by "moving" electrons (orbital magnetization). Since in the CrF_6^{3-} and the $CoCl_4^{2-}$ ions we have orbitally nondegenerate ground states ($^4A_{2g}$ and $^4A_2$, respectively), one can associate the magnetization density very largely with the appropriate one-electron spin density distributions. The spin distribution may be expressed in terms of the partial occupation of molecular orbitals, perhaps accompanied by some polarization of fully occupied orbitals.

Crystals of K_2NaCrF_6 were examined by Wedgwood:[1] polarized neutron scattering by the cubic crystals, held at 4.2 K and placed in a strong magnetic field, was analyzed to discuss spin transfer from the chromium(III) ion to the fluoride ions and the covalence in the Cr–F bonds associated with the transfer. Wedgwood's theoretical analysis was limited to Fourier methods which have well-known disadvantages.

The $CoCl_4^{2-}$ ions in crystals of Cs_3CoCl_5 have been examined even more fully,[2,3] and the crystallography is particularly advantageous in so far as a number of observed magnetic reflexions have intensities due to ligand effects alone; covalence can thus be measured rather more directly.

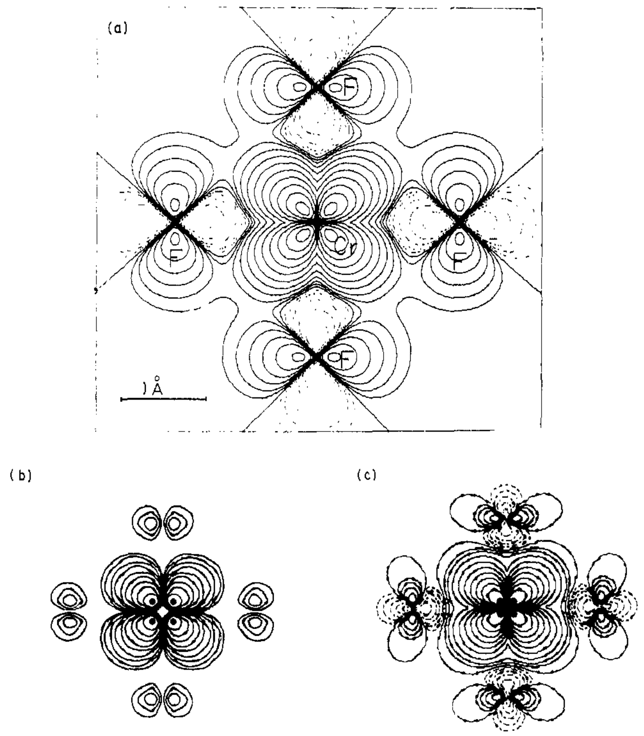

Figure 1. Sections of the residual spin density of the octahedral CrF_6^{3-} ion determined from (a) a multipole analysis[4] of the magnetic structure factors of K_2NaCrF_6 measured by Wedgwood,[1] (b) a restricted Hartree–Fock calculation, and (c) an unrestricted Hartree–Fock calculation by using a double zeta basis. The first continuous contour represents zero spin density. The *n*th contour from the zero contour represents the $\pm 2^{n-1} \times 10^{-3}$ e/Å^3 density contour. The dotted contours represent negative spin density.

We summarize a model which provides experimental spin densities in such a way that it allows immediate comparison with theories of valence. The one-electron density in the unit cell is expressed as a superposition of one-center density functions expanded as a linear sum of density fragments of the type[4]

$$\rho_{lm}(r,\theta,\phi) = M_l^m N_l^m Z_l^m(r,\theta,\phi) R_l(r)/4\pi$$

$$(l = 0, 1, 2, ..., -l \le m \le l)$$

with M, N, and Z being, respectively multipole populations, normalization factors, and Tesseral harmonics; $R(r)$ is the radial wave function for the appropriate center. Symmetry often significantly restricts the number of nonzero multipoles, but, more generally, the multipole populations and the radial exponents are well determined by a least-squares fitting procedure to the observed magnetic structure factors, with the structure factor being recast into the form

$$F_{\text{calcd}}(\mathbf{S}) = \sum_{\text{cell}}\left(\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l M_{j,l}{}^m N_l{}^m 4\pi\langle\mathcal{J}_{j,l}\rangle Z_l{}^m(\alpha,\beta)\exp[-i2\pi\mathbf{h}\cdot\mathbf{x}_j - \mathbf{h}^t\cdot\boldsymbol{\beta}_j\cdot\boldsymbol{h}]\right) \tag{1}$$

$\mathcal{J}_l$ are spherical Bessel functions; $\mathbf{h} = (\bar{h},\bar{k},\bar{l})$ are *Miller* indexes listed with respect to the reciprocal lattice cell edges a^*, b^*, c^*; $\mathbf{x}_j$ and $\boldsymbol{\beta}_j$ are the positional coordinates and mean-square displacement tensor of the center j.

While we have shown[4] that the multipole populations can often be interpreted in terms of "orbital" populations, we demonstrate here the value of constructing the spin density by the superposition of the density fragments within a sphere containing the complex ion. We need the expression

$$\rho(\mathrm{r}) = \sum_{\substack{\textit{sphere}\\ \textit{centers } j}} \sum_{lm} \rho_{lm}{}^j(\mathrm{r} - \mathrm{r}_j) \tag{2}$$

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(1) F. A. Wedgwood, *Proc. R. Soc. London, Ser. A*, **349**, 447 (1976).

(2) B. N. Figgis, P. A. Reynolds, G. A. Williams, R. Mason, A. R. P. Smith, and J. N. Varghese, *J. Chem. Soc. Dalton Trans.*, 2158 (1980).

(3) P. J. Brown, J. B. Forsyth, and R. Mason, *Philos. Trans. R. Soc. London, Ser. B*, **290**, 481 (1980).

(4) J. N. Varghese and R. Mason, *Proc. R. Soc. London, Ser. A*, **372**, 1 (1980).

0002-7863/81/1503-1300$01.25/0

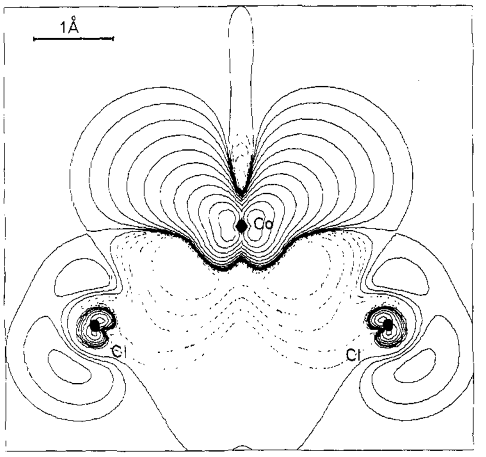

Figure 2. Net spin density of the distorted tetrahedral ($\bar{4}$) $CoCl_4^{2-}$ ion in Cs_2CoCl_5 constructed from a multipole population analysis of magnetic structure factors measured by Figgis et al.[2] The section is the (mirror) plane containing two chlorines and the cobalt center. The contours are in the same intervals as in Figure 1.

which is calculable from the multipoles derived from least-squares analysis. Such an evaluation is not, provided obvious tests are carried out on the completeness of the multipole expansion, subject to the termination effects of a Fourier series based on simple inversion of magnetic structure factors.

The multipole refinement of the Wedgwood data for CrF_6^{3-} has been described fully:[4] the multipole-based spin density synthesis is shown in Figure 1a. The transformation of the multipole populations into "local orbital" populations[4] demonstrated a $t_{2g}^{2.67(1)}$ configuration, a spin density of 0.31 (10) in a metal 4s orbital, and a spin transfer to the fluorines which effectively includes a redistribution of 0.02e from the σ- to the π-bond framework with a negative $p_z[p(\sigma)]$ orbital population of 0.05e (+0.03e in the $2p\pi(x,y)$ orbitals). All of this is clearly indicated in Figure 1a.

Two spin polarized calculations[5,6] give spin transfer coefficients for Cr(III) in CrF_6^{3-}, viz. − 0.022e and +0.026e for $f\sigma^*$ and $f\pi$ from a semi-empirical model and 0.048e and +0.010e from an X–α calculation. Broadly, it appears that the calculations do not adequately reflect the magnitude of exchange correlation effects. We have therefore calculated a molecular spin density within the formalisms of both restricted and unrestricted Hartree–Fock theory and by using a double zeta basis. Full details will be published elsewhere but the two theoretical densities are shown in Figure 1b and 1c. We note the close agreement between the unrestricted Hartree–Fock solution (Figure 1c) and the experimental result (Figure 1a), indicating the sensitivity of the polarized neutron experiment to spin correlation effects, which appear as negative p_z orbital densities. Clearly in this case only unrestricted Hartree–Fock calculations provide sufficiently accurate eigenfunctions to match experiment.

The spin density in the $CoCl_4^{2-}$ ion is shown in Figure 2. The correlation negative spin density separating the spin densities around the cobalt and chlorine atoms is striking. Orbital populations are $t_2^{2.62(7)}$ (cobalt) (the e population is not statistically significant) with chlorine p_x being −0.01 (2) and the (σ) p_y and p_z populations being 0.03 (2) and 0.06 (1), respectively.

We have carried out a similar analysis of the molecular ferromagnet, aquabis(bipyridyl)di-μ-hydroxo-(sulfato)dicopper(II) and have shown[7] how the experimental spin density reflects indirect exchange between the magnetically coupled copper atoms.

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(5) R. D. Brown and P. G. Burton, *Theor. Chim. Acta*, **18**, 309 (1970).
(6) A. Tang Kai and S. Larsson, *Int. J. Quantum Chem.*, **13**, 375 (1978).
(7) B. N. Figgis, R. Mason, A. R. P. Smith, J. N. Varghese, and G. A. Williams, *J. Chem. Soc. Dalton, Trans.*, in press.

Secondary $^2H/^1H$ Isotope Effects on Carbon-13 Chemical Shifts in Cycloalkanes. Downfield Shifts Over Three and Four Bonds

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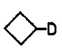
Isotope effects on chemical shifts are well-known[1] but so far have found only limited chemical applications. Mainly two reasons are responsible for this situation: (1) the theoretical interpretation of these parameters in polyatomic molecules is still imcomplete; (2) systematic studies on large systems are rare. Through the introduction of the new generation of superconducting magnets with B_0 fields of up to 10 T, isotope effects transmitted through several bonds can now be measured in a straightforward manner, and new experimental information becomes available. In particular, deuterium isotope effects on carbon chemical shifts are of potential use for spectral assignments, structure determinations, and related investigations.[2] Additional experimental results bearing on these parameters are, therefore, of interest. In this communication we report secondary $^2H/^1H$ isotope effects on ^{13}C chemical shifts for cycloalkanes as measured from the monodeuterated systems **1**–**5**. At the same time the $^{13}C,^2H$ coupling constants of **1**–**5** were determined.

1



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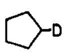

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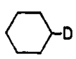

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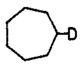

5

1–**5** were synthesized from the corresponding Grignard compounds by hydrolysis, except for **1**, where cyclopropyllithium was the intermediate. In order to allow for an accurate determination of the isotope effect, 4:1 mixtures of the monodeuterated and the isotope–free system were investigated, prepared either by hydrolysis with D_2O/H_2O (4:1) or by mixing. In the case of **1** methanolysis with CH_3OD/CH_3OH (5:1) was employed. ^{13}C NMR spectra were measured at 9.4 T (100.61 MHz) by using the Fourier transform technique. In all cases the chemical shift equivalence of the ring carbons was removed. The assignment of the carbon resonances was based on the triplet splittings due to $^{13}C,^2H$ spin–spin coupling and the order $^1J \gg {}^3J > {}^2J > {}^4J$ valid for these parameters as indicated by the corresponding $^{13}C,^1H$ coupling constants. The results are collected in Table I. In a few cases the $^{13}C,^2H$ splittings measured were corrected for quadrupolar relaxation effects according to the theoretical treatment given by Pople.[3] For this purpose the spin–lattice relaxation times T_1^Q for **2**–**5** were determined by using the inversion recovery technique.

Regarding the isotope effects, the most important new findings are the *downfield shifts* measured for C-3 in **3** and C-4 in **5**. This unusual behavior is most clearly illustrated by a comparison of the spectra of **3** and **4** (Figure 1). So far, the majority of the isotope effects reported were *highfield* shifts, except for a few observations made for carbonyl compounds or deuterated hydroxy groups,[1b,4] where hydrogen bonding is involved. No simple explanation for the exceptional result in the case of cyclopentane

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(1) (a) H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.*, **3**, 63 (1967); (b) W. T. Raynes, *Nucl. Magn. Reson.*, **8**, 12 (1979), see also earlier volumes of this series; (c) C. J. Jameson, *J. Chem. Phys.*, **66**, 4983 (1977).
(2) F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR spectra", Heyden, London, 1978, pp 107–110; P. E. Pfeffer, K. M. Valentine, and F. W. Parrish, *J. Am. Chem. Soc.*, **101**, 1265 (1979).
(3) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

0002-7863/81/1503-1301$01.25/0