Chemistry 543

Spring Semester 1999
First Exam
March 4, 1999

1. Given the complete orthonormal set of functions $\{\alpha,\beta,\gamma\}$ which are eigenfunctions of the z component of angular momentum I_z with eigenvalues $\hbar$, $-\hbar$, and 0, respectively. The operators I^- and I^+ have the following properties:

$$\begin{array}{ll} I^-\alpha = \sqrt{2}\hbar\,\gamma & I^+\alpha = 0 \\ I^-\gamma = \sqrt{2}\hbar\,\beta & I^+\gamma = \sqrt{2}\hbar\,\alpha \\ I^-\beta = 0 & I^+\beta = \sqrt{2}\hbar\,\gamma \end{array}$$

a. Find the matrix representations of the operator I_z , of $I_x \equiv (I^+ + I^-)/2$ and of $I_y \equiv (I^+ - I^-)/2i$ in this basis set.

b. Find the eigenvalues of I_x operator.

2. For the nuclear spin system with two inequivalent sets of nuclei, a single of spin 1/2 and three of a kind also with spin 1/2. (NMR users call this an AB_3 system.) *Determine the NMR Hamiltonian matrix in blocked-out form*, i.e., write all the non-zero elements in terms of the frequencies ν_A, ν_B, and the coupling constant J.

$$\mathcal{H}/h = -\nu_B\,(I_{z(1)}+I_{z(2)}+I_{z(3)}) - \nu_A\, I_{z(4)} + J\,(\mathbf{I}_{(1)}+\mathbf{I}_{(2)}+\mathbf{I}_{(3)})\bullet \mathbf{I}_{(4)}$$

Couplings also exist between B and B nuclei but we ignore these, as they will not affect the spectrum. The operators I_x, I_y, I_z have the following properties:

$I_z(1)\alpha(1) = \frac{1}{2}\hbar\,\alpha(1)$ $\quad$ $I_z(1)\,\beta(1) = -\frac{1}{2}\hbar\,\beta(1)$

$I_x(1)\alpha(1) = \frac{1}{2}\hbar\,\beta(1)$ $\quad$ $I_x(1)\,\beta(1) = \frac{1}{2}\hbar\,\alpha(1)$

$I_y(1)\alpha(1) = \frac{1}{2}i\hbar\,\beta(1)$ $\quad$ $I_y(1)\,\beta(1) = -\frac{1}{2}i\hbar\,\alpha(1)$

$\alpha(1)$ and $\beta(1)$ are functions associated with particle 1.

$\mathbf{I}(1) \equiv I_x(1)\,\mathbf{i} + I_y(1)\,\mathbf{j} + I_z(1)\,\mathbf{k}$ $\quad$ **i**, **j**, and **k** are unit vectors along the x, y, and z directions.

Recall the step up and step down operators:

$$I_\pm \Psi_{I,m} = [I(I+1) - m(m\pm 1)]^{1/2}\hbar\, \Psi_{I,m\pm 1}$$

Remember to use as basis for your representation, the eigenfunctions of

$F_z = F_z(A) + F_z(B)$,

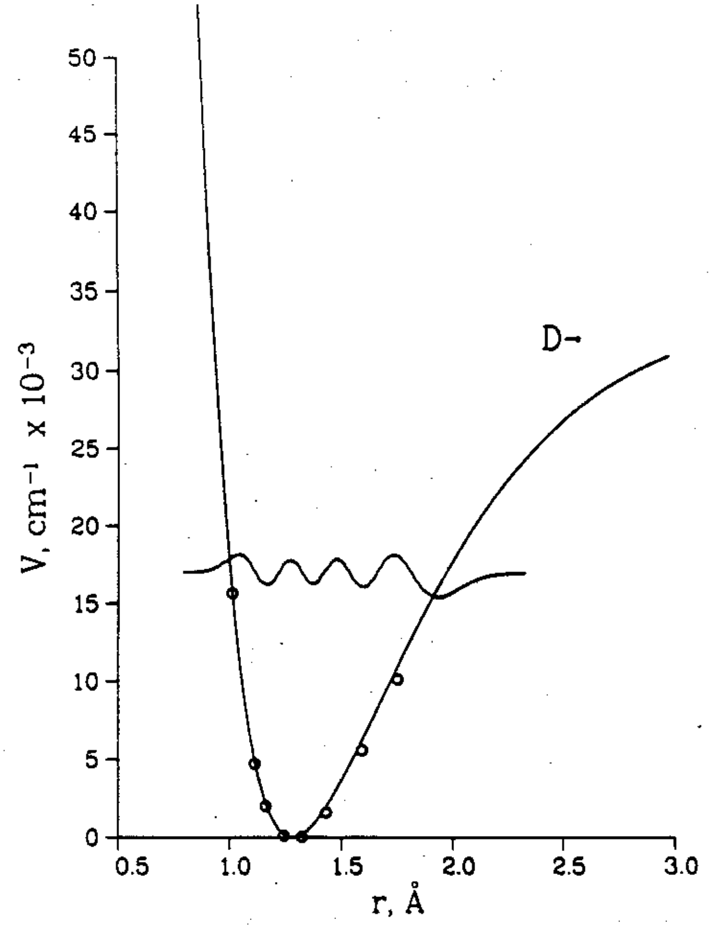
$F_z(B) = I_{z(1)}+I_{z(2)}+I_{z(3)}$.

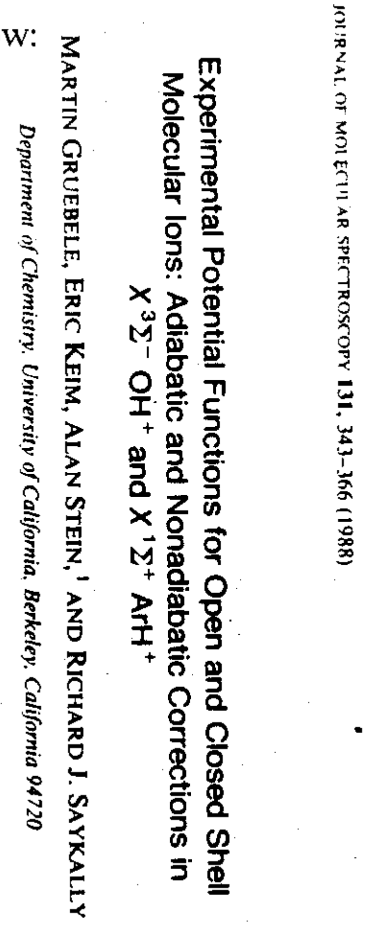
3 The ground electronic state of O_2 is $^3\Sigma_g^-$. What are the results of the following operations on the electronic wavefunction $\Psi(^3\Sigma_g^-)$?

$I\,\Psi(^3\Sigma_g^-)$	inversion of all space-fixed coordinates through the origin
$\sigma_v\,\Psi(^3\Sigma_g^-)$	reflection of molecule-fixed electronic coordinates through a plane containing the internuclear axis
$i\,\Psi(^3\Sigma_g^-)$	inversion of molecule fixed electronic coordinates through the origin (same as inversion of space-fixed electronic coordinates)
$P_{AB}\Psi(^3\Sigma_g^-)$	the interchange of the indistinguishable nuclei A and B
$P_{12}\Psi(^3\Sigma_g^-)$	the interchange of any two electrons

For $^{16}O_2$ molecule, what are the consequences of the nuclear spin of ^{16}O being zero? Apply your discussions specifically to the ground electronic state.

4. The potential function for ArH$^+$ ground state is shown below:




JOURNAL OF MOLECULAR SPECTROSCOPY 131, 343–366 (1988)

Experimental Potential Functions for Open and Closed Shell Molecular Ions: Adiabatic and Nonadiabatic Corrections in $X\,^3\Sigma^-$ OH$^+$ and $X\,^1\Sigma^+$ ArH$^+$

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FIG. 5. Potential functions for ArH$^+$. The solid curve is experimental, circles correspond to points CEPA surface from Ref. (*38*).

The points (circles) are the solutions to electronic motion calculated by Rosmus (1979). The solid curve is derived from a fit to experimental data (312 transitions from microwave, far infrared, infrared , of 5 isotopomers). One of the wavefunctions obtained by numerical solution of the nuclear motion problem is shown at the appropriate energy [Gruebele et al. (1988)] D→ refers to some asymptotic energy on the far right of the figure.

Give specific answers to the following:

a) Give the differential equation that had to be solved in order to find the circles.

b) Give the differential equation that had to be solved numerically to find the wiggly curve? Whaich particular state is this?

c) From the figure you have enough information to estimate the vibrational frequency and D_0 of ArH$^+$ molecule. Do it.

d) What does simple valence bond theory tell us about the stability of the ground states of the rare gas monohydrides (such as ArH) and their ions (such as ArH$^+$)? Explain.

5. Given the following electronic wavefunction of a diatomic molecule:

$$\frac{1}{2}\left\{\pi^{+}(1)\,\pi'^{-}(2)-\pi^{+}(2)\pi'^{-}(1)-\pi^{-}(1)\pi'^{+}(2)+\pi^{-}(2)\pi'^{+}(1)\right\}$$

the π MOs being ungerade. <u>For this electronic wavefunction, determine</u>:

a. total parity

b. the symmetry with respect to interchange of electrons 1 and 2.

c. the symmetry with respect to inversion of electronic coordinates.

d. the symmetry with respect to interchange of the two identical nuclei.

What then is the term symbol? <u>In each case show how you got your answers</u>. <u>Draw a rotational energy level diagram</u> for this state, more or less to scale (neglecting any energy splittings due to angular momentum coupling), for identical nuclei of spin 1/2.

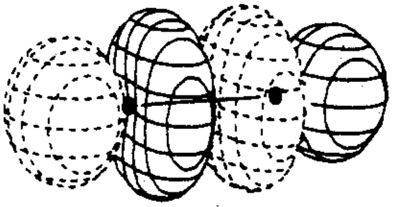
<u>Label</u> each rotational level according to:

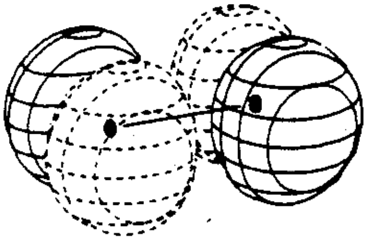
(1) total parity

(2) the symmetry of the space part of the total wavefunction with respect to interchange of the two nuclei

(3) the <u>total degeneracy</u> of each rotational level.

6. The molecular orbitals of a diatomic molecule are shown here. Dashed lines correspond to negative values of the wavefunction. Label each one fully following the usual notation, including the atomic orbitals they come from.





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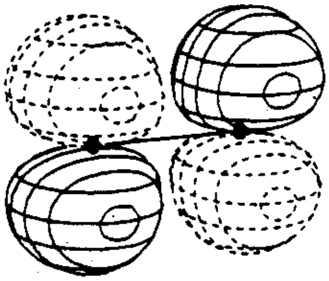

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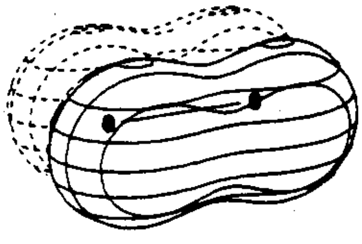

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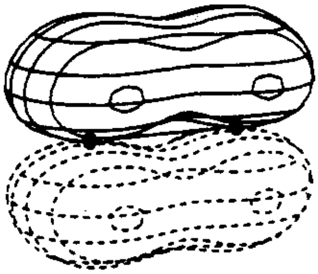

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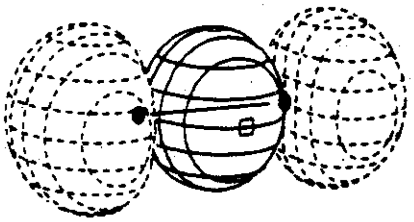

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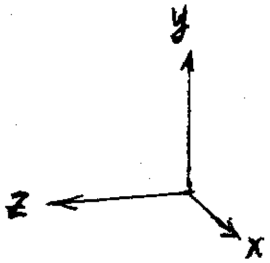

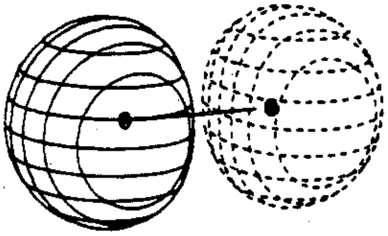

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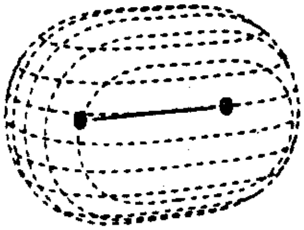

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7.

New Observations on the Visible Spectrum of Antimony Monoxide

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WALTER J. BALFOUR AND RAM S. RAM[1]

A summary of the observed low-lying states of SbO is given in Fig. 1. The ground electron configuration may be written

$$\cdots (z\sigma)^2(y\sigma^*)^2(xp\sigma)^2(w\pi)^4(v\pi^*)^1:\ X^2\Pi \tag{I}$$

with some low-energy configurations being

$$\cdots (z\sigma)^2(y\sigma^*)^2(xp\sigma)^2(w\pi)^3(v\pi^*)^2:\ {}^2\Pi(3),\ {}^2\Phi,\ {}^4\Pi \tag{II}$$

$$\cdots (z\sigma)^2(y\sigma^*)^2(xp\sigma)^1(w\pi)^4(v\pi^*)^2:\ {}^2\Sigma^+,\ {}^2\Sigma^-,\ {}^2\Delta,\ {}^4\Sigma^- . \tag{III}$$

It is probable that the $(xp\sigma)$ and $(w\pi)$ orbitals are similar in energy and bonding powers . The $(w\pi)$ and $(v\pi^*)$ orbitals are relatively bonding and antibonding, respectively, so that the electron promotion from $(w\pi)$ or $(xp\sigma)$ to $(v\pi^*)$ results in a weaker bond.

Derive the given term symbols from the excited electronic configurations

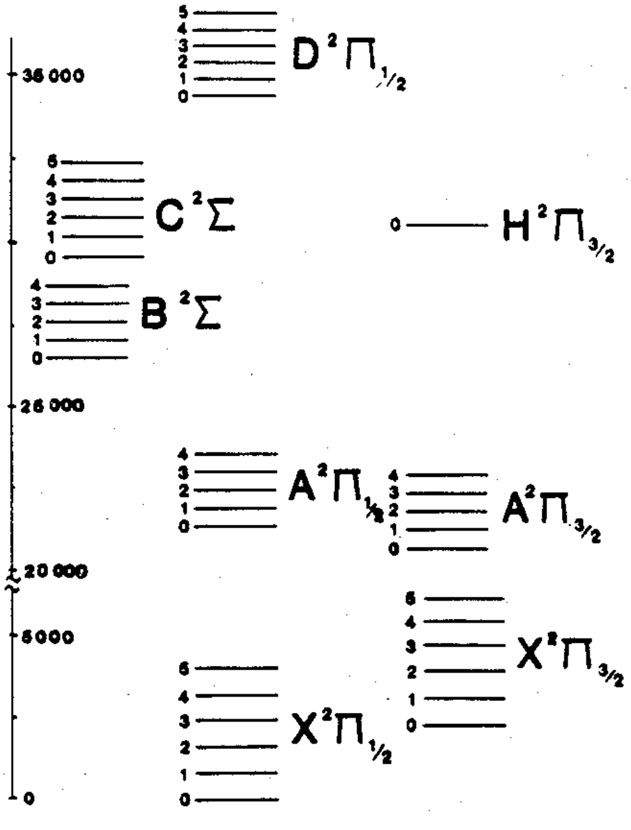
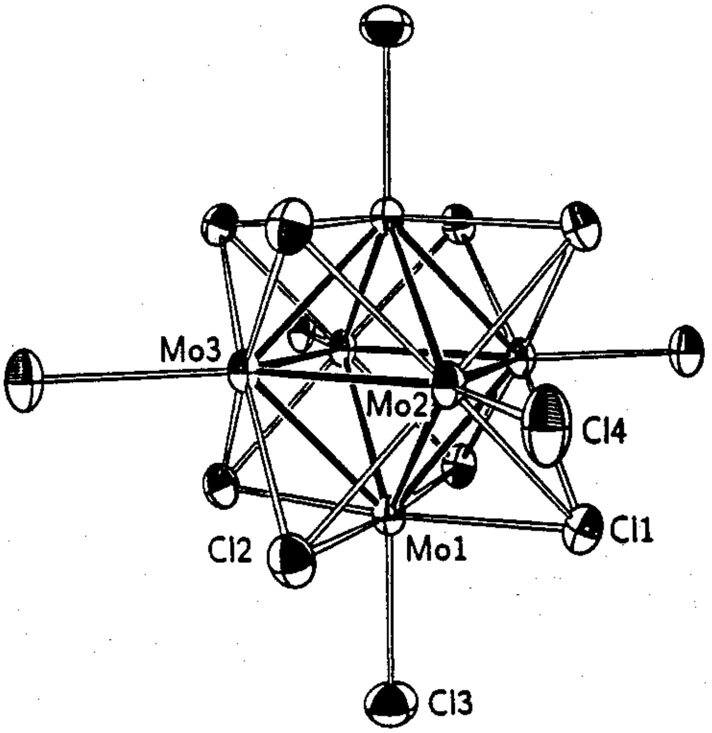


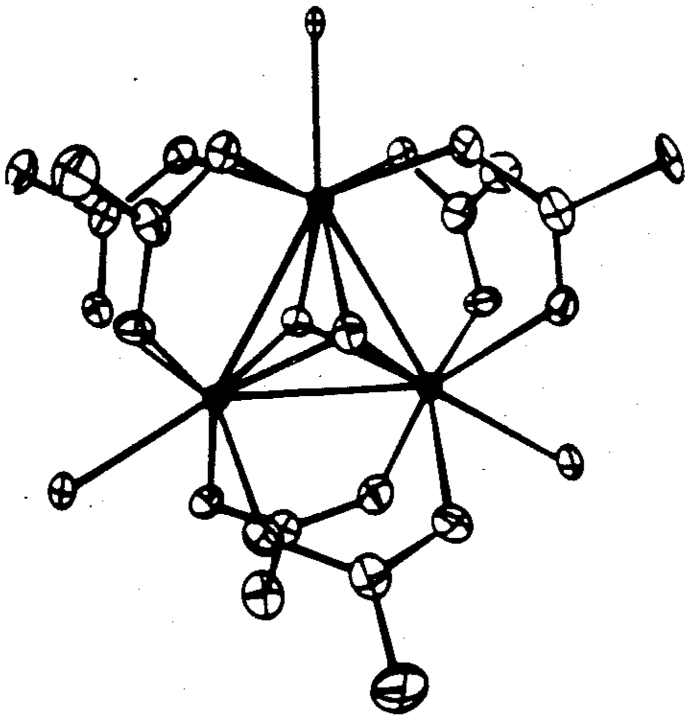
FIG. 1. Observed low-lying states of SbO (in cm^{-1}).

8. Classify the following molecules according to their point group symmetry.

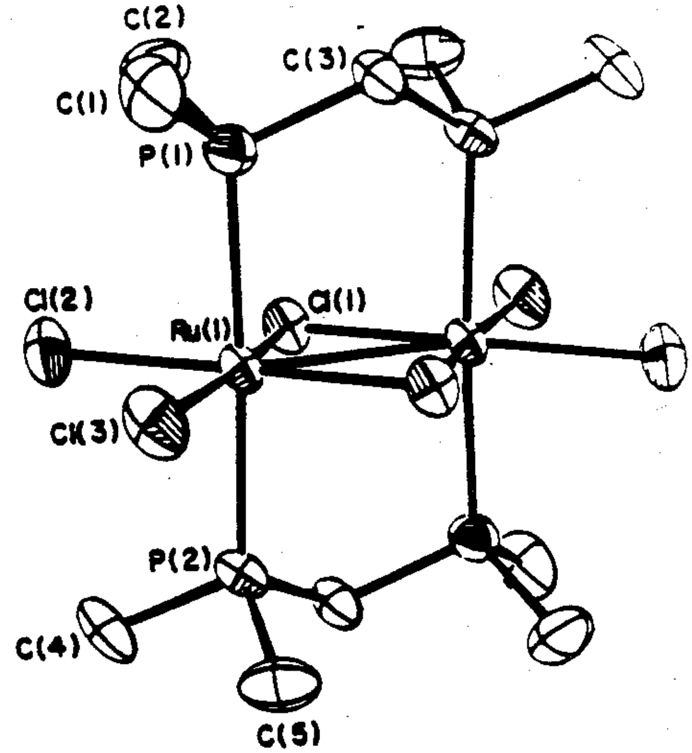
a. Mo_6Cl_{12}



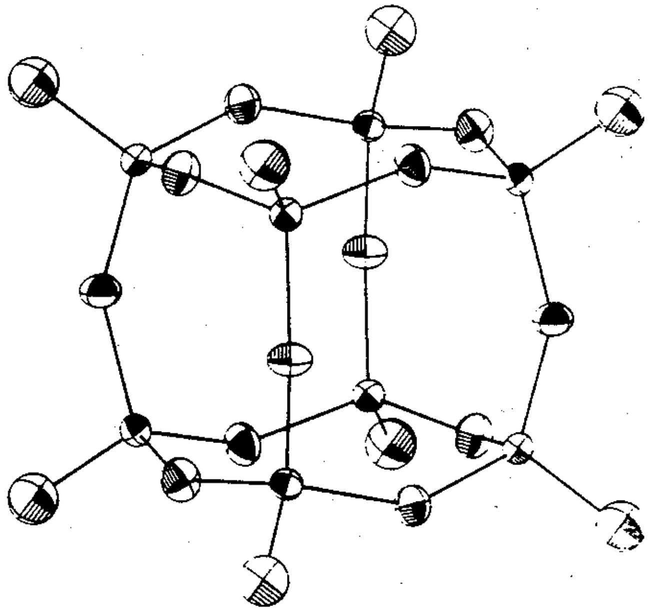
b. $W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$



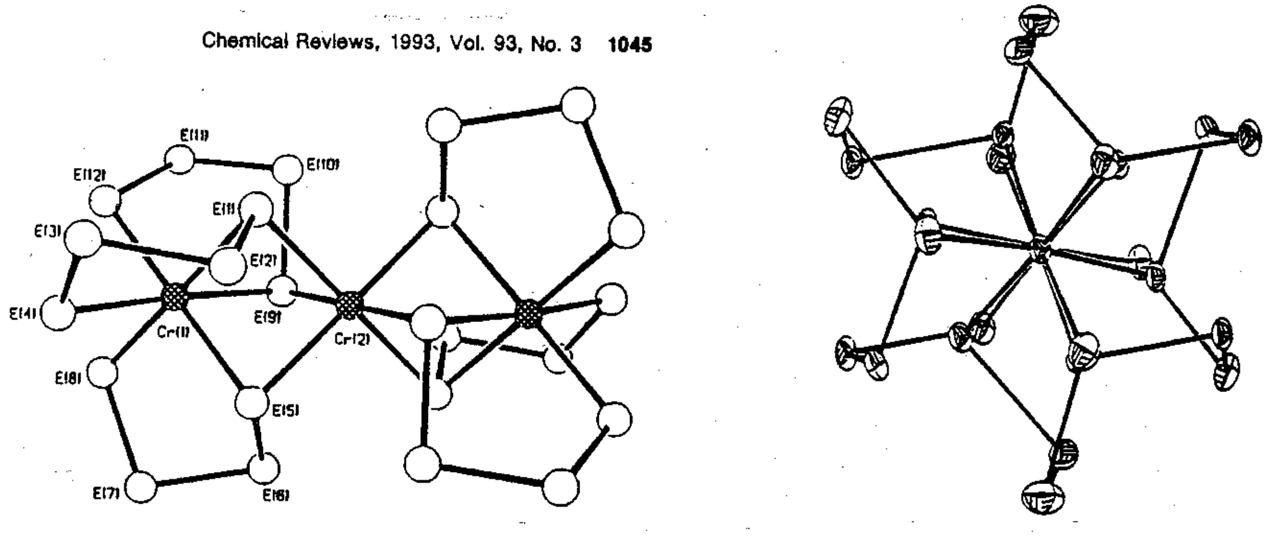
c. $Ru_2Cl_4(dmpm)_2$



d. silasesquioxane $H_8Si_8O_{12}$



e. side and end view of the $[Cr_2E_{24}]^{3-}$ anion, where E is Se or Te (not both)


Chemical Reviews, 1993, Vol. 93, No. 3 1045