isotropic coupling, 16 gauss, observed in the spectrum in Fig. 1. This value is close to those found in several radicals[8] having similar electronic configuration. The isotropic interaction is related to the spin population, a_s^2, of a nitrogen s-orbital by the expression

$$A_{\rm iso} = g_N\beta_N(8\pi/3)|\Psi_{2s}(0)|^2a_s^2$$

where g_N and β_N are the nuclear g-value and magneton, respectively, and $\Psi_{2s}(0)$ is the amplitude of the wave function of the 2s-orbital at the nucleus. Employing[13,14] $|\Psi_{2s}(0)|^2 = 34.0 \times 10^{24}$ cm.$^{-3}$, it is calculated that $a_s^2 = 0.028$ in NF_2. Atkins and Symons[11] found 0.027 for the corresponding quantity in NO_2^{-2}. (The rough nature of such quantitative estimates of relative s and p character has been discussed by Symons.[8])

Assuming that the isotropic fluorine interaction arises from the exchange polarization of a fluorine 2s-orbital, then the preceding expression may be adapted to find b_s^2. The self-consistent field functions for F^- calculated by Löwdin[13] and Allen[15] give an electron density $|\Psi_{2s}(0)|^2 = 11.0$ a.u. at the fluorine nucleus. For an F atom, the density would be 11.5 a.u. Taking the density to lie within the latter range, the calculated fluorine 2s character (b_s^2) is 0.003; the result is small as anticipated.

As in Symon's treatment, a_{pz}^2 may be estimated from Coulson's[16] hybridization relationships and the requirement that the nitrogen's contribution to the $4a_1$ orbital be orthogonal to the NF bond-forming orbitals. From the valence angle,[17] 104°, in NF_2 and the relation

$$\alpha = 2\cos^{-1}(\lambda^2 + 2)^{-1/2} \text{ where } \lambda = a_{pz}/a_s$$

the value for a_{pz}^2 is calculated to be 0.018.

The distribution of unpaired electron spin in the px orbitals (perpendicular to the molecular plane) cannot be determined without experimental knowledge of the anisotropic hyperfine interaction tensor. However, spectra thus far obtained[5] from NF_2 radicals randomly trapped have not been sufficiently informative. By analogy with NO_2^{-2}, a_{px}^2 would be expected to be of the order of 0.50 or greater.

N.m.r. Spectrum

The coupling of the equivalent fluorine nuclei to the nitrogen nuclei in N_2F_4 would be expected to give rise to a triplet in the F^{19} spectrum. However, as in the case of NF_3,[18] at low temperature, the triplet in N_2F_4 has not previously been observed due to quadrupole relaxation. However, when N_2F_4 is dissolved in perfluoro-2,3-dimethylhexane at room temperature, a triplet n.m.r. is observed as illustrated in Fig. 2. The N^{14}–F^{19} coupling constant is ~117 c.p.s., which may be compared[19] with J_{N-F} in the difluorodiazine isomers (145 c.p.s. *cis*, 136 c.p.s. *trans*) and in NF_3 (155 c.p.s.).

Experimental

The e.p.r. spectra reported herein were obtained with a Varian V-4502 e.p.r. spectrometer system employing 100 kc./sec. modulation and detection. The n.m.r. spectrum was obtained on a Varian Associates V-4300 40 Mc./sec. spectrometer. Trifluoroacetic acid (TFA) was the reference used and the shifts noted were downfield from TFA.

Acknowledgment.—This work was performed under Contract No. DA-01-021 ORD-11878.

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Correspondence

The Structure of Triiron Dodecacarbonyl

Sir:

The recent paper by Herber and co-workers[1] which presented evidence for a "staggered" 3–3–3–3[2] structure for triiron dodecacarbonyl ($Fe_3(CO)_{12}$) and for the presence of carbonyl bridges in this complex prompts us to report evidence which also supports this view.

Much of the data which have been reported in regard to the existence of ketone-like carbonyl bridges have been reviewed in Herber's paper. Barraclough and co-workers,[3] however, have reported solvent shift studies in which significant downward shifts in the bridging frequencies for $Co_2(CO)_8$ are observed in more polar solvents, while no such trend is evident for the terminal carbonyl groups of this complex or for $Fe(CO)_5$. That work also pointed out the similarity between the shifts observed for the bridging carbonyl bands in $Co_2(CO)_8$ and those reported[4] for various ketones.

We have extended the solvent shift studies to $Fe_3(CO)_{12}$ and find that the stronger of the two bands in the bridging carbonyl region shifts in much the same manner as do the bridging carbonyl bands in $Co_2(CO)_8$ and in ketones; no studies were made on the other band because of its weak intensity. Table I gives the results for this work which is, we believe, still further evidence for the presence of bridging carbonyl bands in

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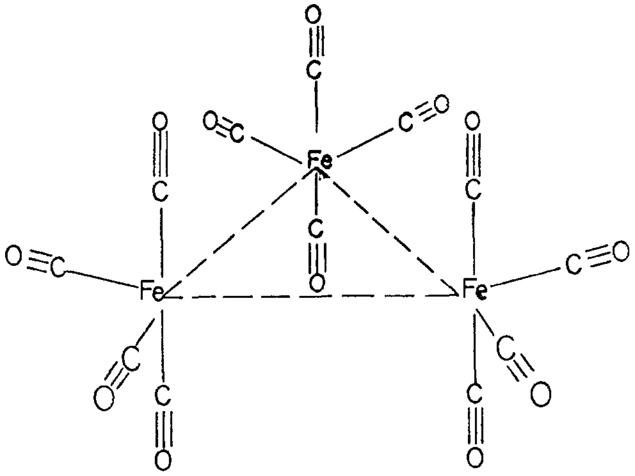

Figure 1.

TABLE I

SOLVENT EFFECTS FOR CARBONYL GROUPS[a]

Solvent	Stretching frequencies, >C=O, cm.$^{-1}$					
	Acetone[4]	Cyclohexanone[4]	Acetophenone[4]	Benzophenone[4]	$Fe_3(CO)_{12}$	$Co_2(CO)_8$
C_6H_{14}	1723	1726	1697	1671	1838	1857[3]
CH_2Cl_2	1713	1708	1685	1660	1825	1846
$CHCl_3$	1712	1705	1684	1658	1826	1845[3]
$CHBr_3$	1708	1701	1681	1656	1824	1840

Solvent	Stretching frequencies, —C≡O, cm.$^{-1}$		
	$Fe(CO)_5$	$Fe_3(CO)_{12}$	$Co_2(CO)_8$
C_6H_{14}	2021[3]	2050[3]	2068[3]
CH_2Cl_2	2022	2051	2076
$CHCl_3$	2019[3]	2051[3]	2071[3]
$CHBr_3$	2018	2048	2074

[a] Due to solvent-induced band broadening in polar solvents resulting in band overlapping, frequency for highest terminal carbonyl only given for each complex.

$Fe_3(CO)_{12}$. Preliminary solvent shift studies on absorptions assigned as combination bands in $Fe(CO)_5$ have yielded no shifts of magnitude and direction comparable to those of the supposed bridging bands. This apparently contradicts the thesis advanced by Cotton and Wilkinson[5] that the low intensity of the two alleged bridging bands in $Fe_3(CO)_{12}$ could better be explained if they were regarded as triple combinations among the metal–carbon frequencies. It should be pointed out that the assigned metal–carbon stretching frequencies for this complex (575 and 594 cm.$^{-1}$) indicate that such triple combinations might more easily yield frequencies of less that 1800 cm.$^{-1}$ while the bridging frequencies are found at 1838 and 1865 cm.$^{-1}$ in *n*-hexane. Finally, it should be noted that the original assignment[6] of the admittedly weak bands in $Fe_3(CO)_{12}$ were not made on the basis of infrared data alone, but in conjunction with an observed ultraviolet band at 2835 Å. in $Fe_3(CO)_{12}$. This band is not observed in the ultraviolet spectrum of $Fe(CO)_5$ and corresponds closely in position and intensity to (n → π*) transitions in ketone carbonyls.

One of the problems which has arisen in the study of the structure of $Fe_3(CO)_{12}$ has been the lack of agreement between infrared data and proposed structures. One hesitates to accept the view of Corey and Dahl[7] that the structure of the complex may be analogous to that which they obtained through X-ray crystallography for $Os_3(CO)_{12}$ (Fig. 1) because of the lack of such agreement. Beck and Lottes[8] have reported seven carbonyl stretching bands for this complex. More recently, Kaesz and Huggins[9] have repeated the work, and report four bands, in agreement with the number required by group theory. Despite the best efforts of many workers, no more than two terminal carbonyl bands have been resolved in $Fe_3(CO)_{12}$. A third, weaker transition at 1997 cm.$^{-1}$ reported by Cotton and Wilkinson has now been shown[10] to be in fact an $Fe(CO)_5$ band produced through the decomposition of $Fe_3(CO)_{12}$ in solution.

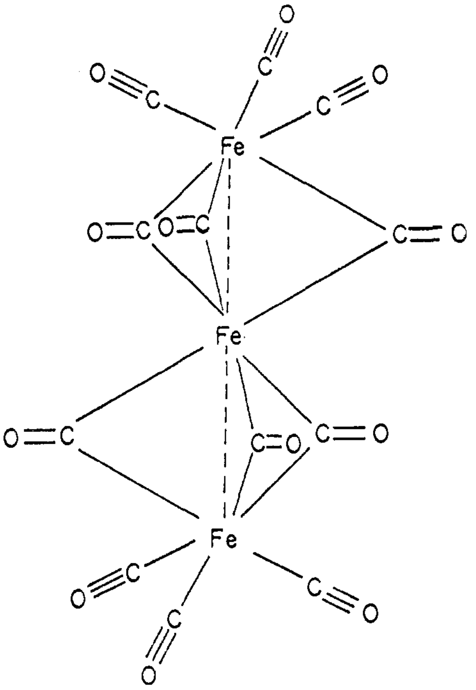

Figure 2.

It has been noted by Cotton and Monchamp[11] that it is often risky to infer structures by comparing observed spectra to those predicted by group theory. Although there have been instances, *e.g.*, in the case of the cobalt carbonyls,[11,12] in which this practice led to erroneous results, we believe that improved instrumentation has somewhat mitigated the danger in recent years and that we may profitably employ it to aid us in the structural determination of $Fe_3(CO)_{12}$. The "staggered" 3-3-3-3 structure (Fig. 2) belongs to the D_{3d} point group and a vibrational analysis leads to the prediction of two active terminal carbonyl stretching vibrations (of A_{2u} and E_u symmetry) and two bridging carbonyl stretches (also A_{2u} and E_u) in agreement with the infrared data.

This structure is analogous to the known structure of $Fe_2(CO)_9$ as determined through X-ray work by Powell

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and Ewens[13] and supported by infrared data.[14] The diverse physical properties of the two carbonyls despite possible structural similarities might be explained in terms of the vacant orbital on the center Fe of $Fe_3(CO)_{12}$ which may, for example, facilitate solvation. No such orbital is available in $Fe_2(CO)_9$. Despite the fact that the weak intensities of the carbonyl bridges have not been satisfactorily explained, we believe the weight of evidence supports the "staggered" 3–3–3–3 structure for $Fe_3(CO)_{12}$.

Acknowledgment.—We wish to thank the United States Atomic Energy Commission for support of this work under contract No. AT-(40-1)-2434.

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RECEIVED MAY 17, 1963

Electronic Spectra of Vanadyl Complexes at Low Temperatures

Sir:

Electronic absorption spectra of various complexes of the oxovanadium(IV) ion, VO^{2+}, have been reported for over a dozen years,[1–19] and several authors[7–9,11,13,16–18] have attempted to assign some of the observed bands to theoretically predicted transitions. Ballhausen and Gray[13] present the most elegant and detailed discussion of the electronic structure of the VO^{2+} ion in a C_{4v} symmetry environment; specifically they treat $VO(H_2O)_5{}^{2+}$. They compare their own experimental data and that of others with calculations from a molecular orbital model. Others have used their model to assign bands observed in the visible and ultraviolet spectra of other vanadyl[16–18] complexes and chromyl and molybdenyl[20] complexes.

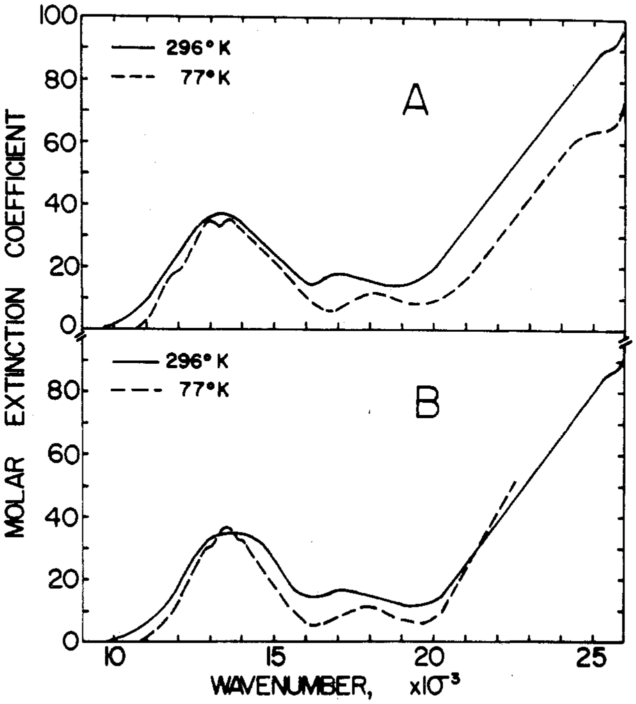

Fig. 1.—The optical absorption spectra of $VO(acac)_2$ dissolved in: A, 3:7 isopropyl alcohol:isopentane; B, 2:5:5 ethanol:isopentane:ether; at 296°K. and at 77°K.

We wish to report our results of preliminary spectral studies of complexes of oxovanadium(IV) ion at low temperatures because these results strongly suggest that while the Ballhausen and Gray[13] model *may* correctly describe the $VO(H_2O)_5{}^{2+}$ ion, the model should be modified before it is generally applied to other vanadyl species, as is currently being done.

In Fig. 1 are shown optical spectra obtained for bis-(acetylacetonato)-oxovanadium(IV), $VO(acac)_2$, in two different solvent media, at both room temperature and liquid nitrogen temperature. The particular solvents (see legend to Fig. 1) were chosen because they solidify to clear glasses at low temperature.[21] The low temperature double beam absorption cell designed and built by Smith, Smith, and McGlynn[21] for use in Beckman DK-1 and DK-2 recording spectrophotometers was used to obtain the spectra reported here. From Fig. 1 and Table I, in which we have listed the values of the band maxima, it is seen that the broad "first band" is resolved into at least three bands at low temperature. The symmetry of $VO(acac)_2$ is no higher than C_{2v} and in such a symmetry the number of crystal field (C.F.) or d–d bands expected is four[17] regardless of whether a simple C.F.[22] or more involved M.O. model is consulted. Therefore we propose that the four relatively low intensity bands ($\epsilon \sim 40$) occurring in the 12,000–18,000 cm.$^{-1}$ range arise from just the expected four d–d transitions. This then implies

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