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Carbon-13 Nuclear Magnetic Resonance Study of the Fluxional Behavior of Cyclooctatetraenetricarbonyliron and -ruthenium

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Abstract: The fluxional behavior of the title compounds has been investigated by ^{13}C NMR. The 1,2 shift mechanism for the ruthenium compound, previously deduced from ^1H NMR spectra, has been confirmed and a new assessment of the activation parameters, which is in satisfactory agreement with the previous one, has been made. The main new result, however, is that for the iron compound, where proton NMR had failed to reveal the mechanism because of the low temperature required to attain the slow exchange limit, the mechanism has now been proved, directly and unambiguously, to be 1,2 shifts. The Arrhenius parameters obtained by a complete line shape analysis are: $E_a = 8.1\ (2)$ kcal and $\log A = 13.5\ (2)$ for the iron compound; $E_a = 8.6\ (1)$ kcal and $\log A = 13.3\ (1)$ for the ruthenium compound. The averaging of the CO signals is also observed in the same general temperature range, but the mechanistic relationship between the two processes is not unambiguously revealed by the available data, contrary to an earlier assertion by others.

One of the earliest fluxional organometallic molecules to be subjected to study by nuclear magnetic resonance spectroscopy was $C_8H_8Fe(CO)_3$, but proton NMR spectra proved unable to resolve the mechanistic problem umambiguously,[1-3] in part because the slow exchange limit was not reached at the lowest practicable temperature of measurement (ca. −150 °C).[3-8] Fortunately, the ruthenium analogue reached the limiting spectrum at about −140 °C, and this spectrum was sufficiently simple to allow mechanistic analysis.[9,10] It was possible to show that rearrangement of $C_8H_8Ru(CO)_3$ takes place by 1,2 shifts and also to make an estimation of the activation parameters, viz., $E_a = 9.4 \pm 0.5$ kcal/mol and $\log A = 14.0 \pm 0.7$. Because of the uncertainties in line widths introduced by the proton-proton coupling, which could only be treated approximately, the true uncertainties in these parameters (the limits quoted reflect only the statistical errors in the least-squares plots) should be two-three times higher than those quoted. Since the 1,2 shift mechanism was found to operate for $C_8H_8Ru(CO)_3$ it was suggested[9,10] that it probably operates also for $C_8H_8Fe(CO)_3$, but this has been only a plausible supposition and not a proven fact.

With the availability of Fourier transform carbon-13 NMR, we were prompted to reexamine $C_8H_8Fe(CO)_3$ and also, for comparison, $C_8H_8Ru(CO)_3$. The advantages of ^{13}C spectroscopy,[11] particularly the greater range (in hertz) of chemical shifts and the absence of spin-spin coupling (if the abundance of ^{13}C is kept low and protons are decoupled) seemed likely to make possible the mechanistic analysis that had not been attainable previously. We have noted a brief report[4] on the ^{13}C spectrum of $C_8H_8Fe(CO)_3$ which showed only that the structure in solution is of the (1-4)-tetrahapto type since a four-signal spectrum for the ring carbon atoms can be observed below −120°. Apparently no mechanistic conclusions were drawn; in any event, none was stated. It was stated that no spectra in the temperature range between −120 and −20° were recorded. We have carried out carbon-13 NMR studies of the rearrangement mechanisms of both the iron and ruthenium compounds and the results are reported in detail here.

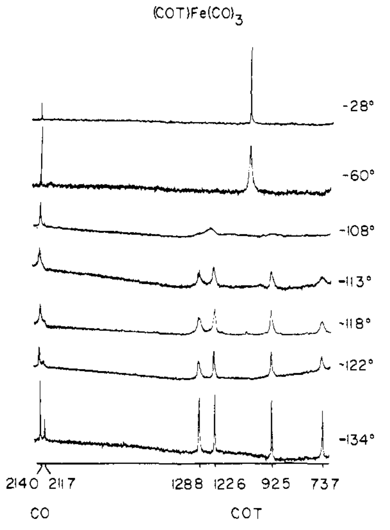

Figure 1. The carbon-13 NMR spectra of $(C_8H_8)Fe(CO)_3$ at various temperatures. Chemical shifts are downfield from tetramethylsilane, ring protons are decoupled, and solvent signals have been omitted for clarity.

Experimental Section

The compounds were prepared by methods described previously,[10,12,13] although for $C_8H_8Ru(CO)_3$ we also used the method of Johnson et al.[14] and of Kruczynski et al.,[15] which gave better yields than the original method of Cotton et al.[10] The newer method, which has not been described in detail, is as follows.

To a three-neck Pyrex flask containing 50 ml of dry, degassed heptane, were added 0.5 g of $Ru_3(CO)_{12}$ and 3.2 ml of cyclooctatetraene. The free volume of the flask was then filled with carbon monoxide and the stirred reaction mixture was maintained at 20-25 °C under irradiation with a 140-W low-pressure Hanovia lamp. In one attempt using benzene as solvent no product was detected after 20 h. The reaction was monitored by following the changes in the CO stretching spectrum.[16] The optimum reaction time seems to be about 45 h, at which time the solution is homogeneous and shows no infrared bands due to $Ru_3(CO)_{12}$. The solution was reduced in volume in vacuo to about 10 ml and chromatographed on Woelm alumina, activity grade II, 1.0 × 40.0 cm, with hexane. The excess COT appeared first followed by a large orange band of (COT)Ru(CO)$_3$. Small amounts of unreacted $Ru_3(CO)_{12}$ remained at the top of the column. The hexane was removed from the (COT)Ru(CO)$_3$ to yield 0.5 g (72% based on Ru) of product. The ir, NMR, and melting point checked with those of a sample prepared by the original method.[4]

The carbon-13 NMR spectra were recorded on a Jeol PFT 100/Nicolet 1080 Fourier transform spectrometer at 25.035 MHz. A sweep width of 6000 Hz, a tilt angle of 23°, and a repetition rate of 1.1 s were employed. The temperatures, measured with a copper-constantan thermocouple inserted into an NMR tube and read on a Leeds and Northrup Model 913 digital thermometer, were constant to ±2°. The spectra from +22 to −90° were recorded in CH_2Cl_2 with acetone-d_6 (10%) and Me_4Si (5%). Below −90°, $CHFCl_2$ was employed as a solvent with either CD_2Cl_2 (15%) or acetone-d_6 (10%) as an internal deuterium lock and Me_4Si (2%) for the internal reference. Below −90° between 25 000 and 35 000 transients were collected, whereas above −90° the solvent mixture allowed greater concentrations of compound to be employed so that only 1000-2000 scans were needed.

The NMR spectra were computer simulated for purposes of line shape analysis using a locally modified form of the program EXCHSYS by G. M. Whitesides and J. K. Krieger.

Results and Interpretation

The proton-decoupled FT carbon-13 spectra of $C_8H_8Fe(CO)_3$ and $C_8H_8Ru(CO)_3$ are shown in Figures 1 and 2, respectively. Solvent signals have been deleted for the sake of clarity. From these data, the following important conclusions may be drawn.

(1) The spectra in the slow exchange limits are in complete accord with the existence in solution of the same structures as found in the crystals of these substances.[8,17] There are four signals with equal intensities in the upfield region, corresponding to the four pairs of equivalent ring carbon atoms and there is a pair of signals downfield, in an intensity ratio of 2:1 corresponding to the carbonyl carbon atoms.

(2) At the higher temperatures all ring signals have coalesced to a singlet and, likewise, the carbonyl signals have become a singlet.

(3) The *initial rates of broadening* of the ring signals are *unequal.* Two of them broaden more quickly than the other two. This demonstrates that the process by which the ring carbon atoms achieve time-average equivalence is one in which two environments afford greater residence times than the other two. Thus, for the $(\eta^4\text{-}C_8H_8)M(CO)_3$ molecules, in contrast to the $(\eta^6\text{-}C_8H_8)M(CO)_3$ molecules,[18] any random exchange process, a process with a symmetrical intermediate or transition state, and also the 1,3 shift process (vide infra) are all rigorously excluded. The possibility of 1,5 shifts can also be dismissed since this would lead to a high temperature spectrum consisting of two lines rather than one.

(4) It can be shown that the mechanism of rearrangement is a series of omnidirectional 1,2 shifts of the $M(CO)_3$ group relative to the C_8H_8 ring, by arguments now to be given. Figure 3 gives a diagram in which the carbon atoms are numbered *1-8*, the positions for the metal atom are numbered **1-8**, and the distinct sites for the carbon atoms are labeled *a, b, c, d*, for the case where the metal atom occupies position **1**.

For the three discrete 1,*n* shift processes (*n* = 2, 3, 4) that are consistent with the attainment of a one-line spectrum in the fast exchange limit, the manner in which the carbon nuclei, *1-8*, are permuted among the types of sites, *a-d*, can be conveniently expressed by the following permutation schemes. In each case the first row lists the initial allocation of the nuclei (in numerical order, *1-8*) to the types of site and the second row gives the new site occupancies for the nuclei, in the same numerical order, after the 1,*n* shift has occurred.

$$\left.\begin{array}{cccccccc} a & b & c & d & d & c & b & a \\ b & c & d & \underline{d} & c & b & a & \underline{a} \end{array}\right\} 1,2$$

$$\left.\begin{array}{cccccccc} a & b & c & d & d & c & b & a \\ b & a & a & b & c & d & d & c \end{array}\right\} 1,3$$

$$\left.\begin{array}{cccccccc} a & b & c & d & d & c & b & a \\ c & \underline{b} & a & a & b & \underline{c} & d & d \end{array}\right\} 1,4$$

It can easily be seen that for the 1,3 shift, every nucleus changes its environment whereas for 1,2 and 1,4 shifts there are two (underlined) which do not. Thus, as already noted, 1,3 shifts are inconsistent with observation, since all lines would begin to broaden at the same rate for this process. Both 1,2 and 1,4 shifts would produce the type of behavior observed since, for each, there are two sites (*a* and *d*, for 1,2; *b* and *c* for 1,4) for which the mean residence time is twice as long as it is for the other two. A decision between 1,2 and 1,4 shifts requires an assignment, or at least a partial assignment. Fortunately, it is possible to make the necessary assignments with confidence.

For C_8H_8 and other nonaromatic polyenes (e.g., various 1,3-dienes), the ^{13}C signals occur 120-140 ppm downfield (from Me_4Si).[19] For C_8H_8 itself,[18] the signal occurs at about 133 ppm (varying slightly with solvent). Thus the two signals at 122.6 and 128.8 ppm in $C_8H_8Fe(CO)_3$ and the

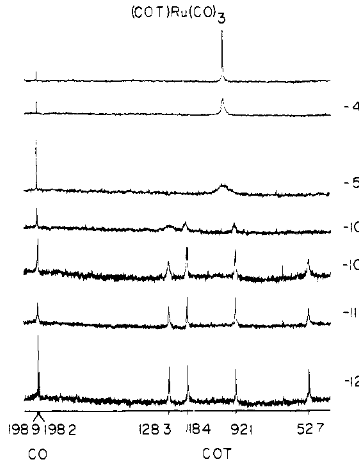

Figure 2. The carbon-13 NMR spectra of $(C_8H_8)Ru(CO)_3$ at various temperatures. Chemical shifts are downfield from tetramethylsilane, ring protons are decoupled, and solvent signals have been omitted for clarity.

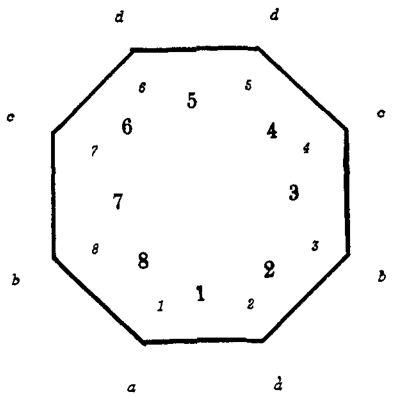

Figure 3. A diagram showing how the eight (formal) positions for the metal atom, **1-8**, and the eight ring carbon atoms, *1-8*, may be labeled. The four types of ring atom site, *a, b, c, d*, are then labeled as they would occur with the metal atom occupying position **1**.

Table I. Activation Parameters

	(COT)Fe(CO)$_3$ COT	(COT)Fe(CO)$_3$ CO	(COT)Ru(CO)$_3$ COT	(COT)Ru(CO)$_3$ CO
E_a	8.1 (2)	8.3 (9)	8.6 (1)	8.9 (7)
Log A	13.5 (2)	13.3 (9)	13.3 (1)	13.2 (4)
$\Delta H^‡$	7.8 (2)	8.0 (9)	8.3 (1)	8.6 (7)
$\Delta S^‡$	3.0 (9)	3 (6)	2.0 (8)	2 (4)
$\Delta G_{25°}{}^‡$	6.8 (3)	7 (2)	7.7 (3)	8 (1)

analogous ones at 118.4 and 128.3 ppm in $C_8H_8Ru(CO)_3$ can be confidently assigned to the *c* and *d* carbon atoms. It is also well established that coordination of a 1,3-diene to $Fe(CO)_3$ causes an upfield shift of the resonances of the four diene carbon atoms, and that the outer ones (those of type *b* in Figure 3) shift about 40 ppm more than the inner ones (those of type *a* in Figure 3).[20-22]

It is, therefore, clear that the correct assignment of the four ring carbon signals in the low-temperature spectra of both compounds is, from left to right: (*c, d*), *a, b*, where the order of *c* and *d* is undetermined as yet. However, this partial assignment is sufficient to select the mechanism, since 1,2 shifts require the *a* resonance to broaden more slowly than the *b* resonance, whereas the 1,4 mechanism requires the converse. It then follows that the correct choice for resonances due to the *c* and *d* sites is such that the complete assignment (left to right) is *c, d, a, b*.

The 1,2 shift mechanism thus inferred for $C_8H_8Ru(CO)_3$ is in accord with the earlier result[9,10] derived from the ^1H spectra for that compound, and the mechanism for $C_8H_8Fe(CO)_3$ is now directly revealed for the first time.

(5) By calculating spectra for various rates of the 1,2 shift process and matching calculated spectra to those observed at various temperatures, the activation parameters for the 1,2 shift processes have been evaluated. Since in each case the lines in the lowest temperature spectra recorded were not fully narrowed, we used for them the widths of the singlet at the highest temperature. The activation parameters obtained are listed in Table I.

It is satisfying to find that the results obtained here for $C_8H_8Ru(CO)_3$ are in satisfactory agreement with those previously derived[10] from the ^1H spectra and quoted in the introductory section. Thus, we have E_a (^{13}C) = 8.6 (1) kcal/mol, E_a (^1H) = 9.4 ± 1.5 kcal and log A (^{13}C) = 13.3 (1), log A (^1H) 14.0 ± 2.1, where we attach realistic limits of error to the ^1H values, as explained earlier. The activation energies (E_a or $\Delta H^‡$) for the iron compound are estimated to be about 0.5 kcal/mol smaller than those for the ruthenium compound, while the log A or $\Delta S^‡$ values differ insignificantly. This small difference is in accord with the small but crucial difference in the temperatures at which slow exchange ^1H spectra can be observed and thus with the previous impossibility of directly resolving the problem of mechanism for the iron compound using proton spectra.

(6) Line shape analysis for the carbonyl resonances is considerably less accurate than for the ring resonances since the chemical shift differences involved are much smaller (6-20 Hz vs. 1400-1900 Hz) and the temperature range over which the entire process of transformation from a two-line spectrum to a one-line spectrum occurs is very small. Since many of the errors involved will be similar in the two compounds, the indication that carbonyl scrambling has a higher activation energy in the $Ru(CO)_3$ group than in the $Fe(CO)_3$ group is probably reliable. Such a relationship is in accord with results we have obtained in other cases.[23]

Unfortunately, in these systems, the activation parameters for the two processes within a given molecule (CO scrambling and "ring-whizzing") are so similar and have sufficient margins of error that it is impossible to say whether the two processes are truly simultaneous (and therefore, *possibly*, interdependent) or not. We cannot agree with the previous assertions[4] that line shape analysis "leads to significantly lower rate constants" for the carbonyls and that "the carbonyl exchange process is independent of the ring-atom exchange process," in the sense that the latter conclusion is an unambiguous result, not subject to doubt. We shall discuss this point below.

Discussion

Finally, some 13 years after the first report[8] that $C_8H_8Fe(CO)_3$ is a fluxional molecule, we have the first and only direct, unequivocal, and quantitative characterization of the process responsible. It had, of course, previously been inferred from the ^1H NMR study of $C_8H_8Ru(CO)_3$ that the iron compound would execute 1,2 shifts, with an activation energy of <9.4 kcal/mol, but that extrapolation has now been independently proven correct and made quantitative. Also, the conclusions from the ^1H NMR analysis of $C_8H_8Ru(CO)_3$ have been independently verified, and the accuracy of the activation parameters has been improved.

As noted under point 6 above, the temperature range and inferred activation parameters for scrambling of the CO groups in these molecules so closely correspond to the temperature range and activation parameters for the 1,2 shifts that it is impossible to say whether they are mechanistically coupled or not. It seems likely, however, that the apparent

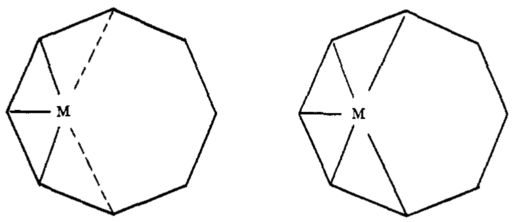

Figure 4. Schematic transition states for 1,2 shift processes in η^4-$C_8H_8M(CO)_3$ molecules (left) and η^6-$C_8H_8M(CO)_3$ molecules (right).

simultaneity here is accidental when observations for other systems are taken into account. It is well known[22,24] that in (diene)$Fe(CO)_3$ systems where no ring-whizzing is possible, CO scrambling occurs in roughly the same temperature range and with similar activation parameters. Indeed the occurrence of scrambling in $M(CO)_3$ systems is so general,[18,25-29] regardless of the nature of the organic moiety connected to it, that it is clear that such scrambling *need not* be caused or induced by any other rearrangement process. It is, of course conceivable that in a molecule where the ring whizzing process is more facile than the CO scrambling process, the former could induce the latter, but no such case has yet been reported, so far as we know.

Finally, it is appropriate, now that the mechanism of "ring-whizzing" in $(C_8H_8)Fe(CO)_3$ and its ruthenium analogue has been conclusively established, to comment on the difference between these $(\eta^4$-$C_8H_8)M(CO)_3$ systems and the $(\eta^6$-$C_8H_8)M(CO)_3$ systems which have recently been shown[18] to rearrange by a quite different mechanism, namely, by way of a symmetrical ("piano stool") intermediate or transition state.

One facet of this comparison can be treated straightforwardly. It is easy to understand why the mechanism with a symmetrical "piano stool" intermediate would not be expected for the $(\eta^4$-$C_8H_8)M(CO)_3$ systems, even though it occurs for the $(\eta^6$-$C_8H_8)M(CO)_3$ compounds.[30] In the "piano stool" intermediate the C_8H_8 ring is flat, or nearly so, and the eight π electrons would be delocalized. In simple MO theory[31] they would occupy the π MO's to give the configuration $a_1^2e_1^4e_2^2$. In the symmetrical $C_8H_8M(CO)_3$ structure, with local C_{8v} symmetry for the C_8H_8M portion, the e_2 orbitals presumably combine with metal d orbitals of e_2 symmetry to form a strong ring to metal bond. The e_1 orbitals presumably also interact with metal d orbitals of e_1 symmetry to form another bonding MO, probably even more stable than the e_2 bonding MO. In the case where M in $M(CO)_3$ is Cr, Mo, or W, one then has an 18-electron configuration *plus* the two ring a_1 electrons. Since these two electrons occupy the most stable orbital of the ring system and also because the a_1 orbitals of the metal atom (d_{z^2}, p_z, s) may be used in bonding to CO groups and are also not adapted to overlap well with the large circular a_1 orbital of the ring, this pair of a_1 ring electrons is essentially nonbonding and does not, therefore, have a seriously destabilizing effect.

However, when there is still another pair of electrons in the molecule, as is the case when M = Fe, Ru, Os (which have two more electrons than Cr, Mo, and W, respectively) the symmetrical arrangement is seriously destabilized because these two electrons must occupy some distinctly antibonding orbital. It is reasonable to suppose that the destabilizing effect could amount to 20 kcal/mol or more, thus putting the "piano stool" intermediate entirely out of range for the systems whose ground state structures are of the $(\eta^4$-$C_8H_8)M(CO)_3$ type.

The second point of comparison is less easily rationalized. We note that for the $(\eta^6$-$C_8H_8)M(CO)_3$ systems the activation energies (to attain the symmetrical transition state) must be around 6 kcal/mol higher than those for rearrangement via the 1,2 shift mechanism for the $(\eta^4$-$C_8H_8)M(CO)_3$ molecules, since the coalescence temperatures are ~130° (for Cr vs. Fe) and ~110° (for Mo vs. Ru) higher. Since the Cr and Mo compounds employ the "piano stool" rather than the 1,2 shift mechanism, the activation energies for the latter must be at least 1-2 kcal/mol higher. Thus, we would estimate that for the $(\eta^6$-$C_8H_8)M(CO)_3$ species with M = Cr, Mo, the activation energies for 1,2 rearrangements must be about $8.5 + 6.0 + 1.5 = 16$ kcal/mol, or higher. This estimate is in fair accord with the measured activation energies[32] for the $(\eta^6$-$(CH_3)_4C_8H_4)M(CO)_3$ compounds, which rearrange by a restricted 1,2 shift process. The measured values are 15-16 kcal/mol. The question that then arises is: Why is the transition state for 1,2 shifts so much more accessible—by at least 7.5 kcal/mol—for $(\eta^4$-$C_8H_8)M(CO)_3$ systems than it is for $(\eta^6$-$C_8H_8)M(CO)_3$ systems?

There are so many unknown details of the structure of the transition state for 1,2 shifts, that an analysis of this question is bound to be very speculative and therefore subject to the first law of well-regulated discourse.[33]

We may for simplicity assume that in each case, i.e., in both $(\eta^4$-$C_8H_8)M$ and $(\eta^6$-$C_8H_8)M$ systems, the ring system becomes dihedral and the metal atom becomes centered over a coplanar set of three carbon atoms for the η^4 case and five carbon atoms for the η^6 case. Neither of these assumptions is likely to be strictly true. With these assumptions, the transition states will be as represented in Figure 4. On this basis one might argue that for the η^4 system the transition state allows strong interaction with three carbon atoms of the allyl-like system, plus two weaker interactions with adjacent carbon atoms. Thus, the loss of M-C bond energy is not great since it changes from four M-C bonds to three plus two weak ones. For the η^6 systems, however, the transition state allows five M-C interactions, but probably no further ones of any significance since the metal atom cannot approach the carbon atoms adjacent to the 5-carbon chain to which it is primarily bonded without moving away from the center carbon atom of that 5-carbon chain to such an extent that there would be little if anything to be gained. Thus we are suggesting a way to understand why it is more costly in M-C bond energy for the η^6 system to achieve a transition state appropriate to 1,2 shifts than it is for the η^4 system. We hasten to add that there may also be differences in the intrinsic bonding capabilities of the C_3 and C_5 systems based on the properties of their pπ orbitals which could also have an important influence on the stabilities of the two states relative to their respective ground states.

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(30) The reasoning used to justify, or rationalize its occurrence for the $(\eta^6\text{-}C_8H_8)M(CO)_3$ species is such that it would be predicted to occur in $(\eta^6\text{-}C_8H_8)ML_n$ species in general, and also in $(\eta^5\text{-}C_7H_7)ML_n$ species. These predictions are being tested by F.A.C. and John R. Kolb.
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Calculation of the Ground State Electronic Structures and Electronic Spectra of Di- and Trisulfide Radical Anions by the Scattered Wave–SCF–Xα Method

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Abstract: In order to get additional, and independent, evidence concerning the identity of the S_n^- species responsible for the blue color of lapis lazuli, sulfur-doped alkali halide crystals, and certain solutions of sulfur in alkalies, the SCF-scattered wave-Xα method has been used to calculate the ground state electronic structures and the electronic absorption spectra of S_2^-, S_3^-, and S_3^{2-}. The latter was used as a check on the method, and excellent agreement between the observed (~24 000 cm^{-1}) and calculated (~24 500 cm^{-1}) energies of the lowest allowed singlet-singlet electronic absorption band was obtained. For the S_2^- and S_3^- species the first allowed doublet-doublet transition is predicted to occur at 17 300-20 300 cm^{-1} (depending on structure parameters) and 12 000-13 200 cm^{-1} (again depending on structure parameters). Since the blue sulfur-containing systems have an absorption band with an origin at ca. 13 500 cm^{-1} we conclude that the blue chromophore is S_3^-. Likewise, sulfur-doped alkali halide crystals that are pink have an absorption band with an origin at ca. 21 000 cm^{-1} so that the pink color may be attributed to the presence of S_2^-.

The problem we are addressing here has a history dating from the time of Marco Polo (1271) and before. This is the question of how to account for the deep blue color of minerals known from early times as lapis lazuli, and, in the synthetic forms now available, as ultramarine. These substances have long been prized for their beautiful color, and lapis lazuli is still collected from nature today, the principal regions of occurrence being Badakhshan in northeast Afganistan and near the western end of Lake Baikal in the USSR.

In recent times it has been established that the principal component of lapis lazuli and ultramarines is a silicate mineral of the sodalite type[1] containing small amounts of sulfur. It has also been known for some time that a blue color develops when sulfur is heated with water and a trace of basic salt.[2-4] Blue solutions are also formed by sulfur in alkali halide melts,[5,6] on dissolving alkali polysulfides in basic solvents such as dimethylformamide[7,8] and dimethyl sulfoxide,[9] upon doping sulfur into borate glasses,[10] upon electrochemical reduction of S_8 in dimethyl sulfoxide,[11,12] and upon heating alkali halide crystals in sulfur vapors,[13,14] although with some crystals a pink color rather than the deep blue color is formed. In all cases which have been examined spectrophotometrically, the cause of the blue color has been shown to be an absorption band centered at about 625 nm (16 000 cm^{-1}).

Efforts to identify the species responsible for the blue color have been numerous. Lux and co-workers[7,9] attributed it to neutral molecules S_x, $x = 2, 3, 4$. Merritt and Sawyer[11] once suggested that S_8^- is the species formed by electrochemical reduction of elemental sulfur in dimethyl sulfoxide but later retracted[15] this suggestions and agreed with Bonnaterre and Cauquis[12] who showed that the oxidation number in this system is $-\frac{1}{3}$ and proposed S_6^{2-} as the chromophore. Chivers and Drummond[16,17] agreed that the blue species corresponds formally to S_6^{2-} but proposed that its real identity is S_3^-. Gruen, McBeth, and Zielen[6] also propose that the blue color is caused by S_3^-, but Giggenbach[4,8,10] has argued in favor of S_2^-. Hofmann et al.[18] in discussing ultramarine specifically suggest that either S_2^-