Inorg. Chem. **2002**, *41*, 2848–2854

Occupancy of the Sodalite Cages in the Blue Ultramarine Pigments

N. Gobeltz-Hautecoeur,[†,‡] A. Demortier,[†] B. Lede,[†] J. P. Lelieur,*[,†] and C. Duhayon[‡]

Laboratoire de Spectrochimie Infrarouge et Raman (UMR 8516 CNRS), 13 rue de Toul, 59046 Lille Cedex, France, and Holliday Pigments International S.A., 203 Route de Wervicq, BP 17, 59559 Comines Cedex, France

Received August 1, 2001

A quantitative EPR study of blue ultramarine pigments has been performed in order to determine the concentration of the S_3^- chromophore. Copper sulfate $CuSO_4 \cdot 5H_2O$ has been used as a standard, while a ruby crystal was used as an inner standard to take into account the changes of the quality factor of the cavity. These experiments show that, in the most-colored pigments, less than half of the sodalite cages are occupied by a S_3^- radical. In other experiments, it has been shown that the blue ultramarine pigments can be significantly modified by heating under a dynamic vacuum. The concentrations of S_3^- and S_2^-, as deduced from EPR and Raman experiments, are increased after this type of treatment. These changes imply that sulfur species are transformed into S_3^- or S_2^- during this treatment. It is discussed that these sulfur species could be S^{2-}.

Introduction

The ultramarine pigments are a family of mineral pigments characterized by the sodalite structure[1−4] and colored sulfur species encapsulated inside. This three-dimensional structure is composed of close-packed cubooctahedra $(Al_3Si_3O_{12})^{3-}$ called β cages (Figure 1).

Three sodium cations are encapsulated in each β cage (Figure 2) to neutralize the deficit of positive charges induced by the substitution of Si by Al.[5,6] The chromophores of the ultramarine pigments are inserted in the β cages. Blue, green, violet, and pink ultramarines can be found.[3] In this work, we will consider only the blue ultramarines. The blue color is due to the S_3^- chromophore.[7] It has been shown that the blue ultramarine pigment not only contains the blue chromophore but also contains a yellow one which is S_2^-. However, S_3^- is predominant.[8] These polysulfides are encapsulated in the sodalite cages as NaS_3 and NaS_2 salts so that S_3^- and S_2^- are tetrahedrally coordinated to four Na^+ cations (Figure 2). The general formula, $Na_6(Al_6Si_6O_{24}) \cdot 2NaS_x$,[3] corresponds to two β cages of an ultramarine pigment; therefore, the theoretical maximum insertion of the chromophores is 1 S_x^-/β cage ($x = 2$ or 3). To determine the real insertion content, it is necessary to measure the absolute concentration of each chromophore in the pigment.

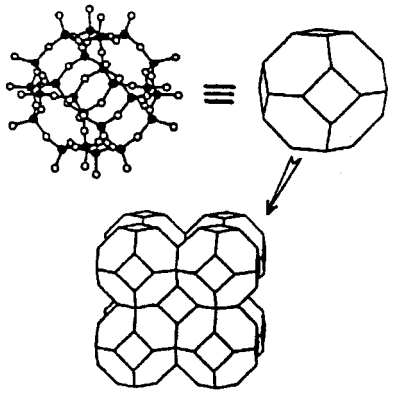

Figure 1. Sodalite structure composed of β cages.

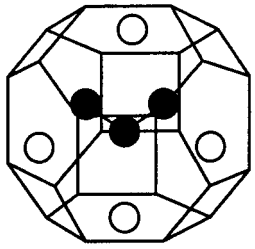

Figure 2. Blue chromophore S_3^- (●) encapsulated in the β cages and surrounded by four sodium cations (○).

* Author to whom correspondence should be addressed. E-mail: jean-pierre.lelieur@hei.fr.
[†] Laboratoire de Spectrochimie Infrarouge et Raman.
[‡] Holliday Pigments International S.A.

(1) Jaeger, F. M. *Trans. Faraday Soc.* **1929**, *25*, 320.
(2) Pauling, L. *Z. Kristallogr.* **1930**, *74*, 213.
(3) Seel, F. *Stud. Inorg. Chem.* **1984**, *5*, 67.
(4) Reinen, D.; Lindner, G. G. *Chem. Soc. Rev.* **1999**, *28* (2), 75.
(5) Barrer, R. M. *Hydrothermal Chemistry of Zeolites;* Academic Press: London, 1982.
(6) Breck, D. W. *Zeolite Molecular Sieves;* Wiley: New York, 1974.
(7) Morton, J. R. *Proc. Colloq. AMPERE* **1969**, *15*, 299.
(8) Clark, R. J. H.; Cobbold, D. G. *Inorg. Chem.* **1978**, *17*, 3169.

10.1021/ic010822c CCC: $22.00
Published on Web 04/30/2002

Few papers on the content of the sodalite cages in the blue ultramarine pigments have been published. In 1978, the Raman experiments of Clark et al. demonstrated that the blue pigment contained both S_3^- and S_2^-. Clark noted that S_3^- was predominant,[8] but no figure was given. Determining the absolute concentration of S_3^- is not very easy. The Raman spectroscopy detects the vibration bands of both S_2^- and S_3^- under resonance conditions.[8−10] This spectroscopy, with the ratio of the intensity of the 545 cm^{-1} band of S_3^- to that of the 590 cm^{-1} band of S_2^-, allows the determination, for a given excitation line, of a quantity proportional to the ratio of $[S_2^-]$ to $[S_3^-]$, but it does not allow the determination of either $[S_2^-]$ or $[S_3^-]$, because the Raman scattering cross section of these species cannot be determined. However, the quantity proportional to $[S_2^-]/[S_3^-]$ can be compared between various samples or for a given sample after various treatments.

The chemical analysis of the pigment, after the destruction of the sodalite structure in an acidic aqueous solution, can only reveal the total content of sulfur, because the sulfur species are hydrolyzed or oxidized in various chemical species (sulfate, thiosulfate, etc.).

The best method for determining the absolute concentration of S_3^- seems to be EPR spectroscopy. At room temperature, it only detects the S_3^- radical at $g = 2.028$, because the EPR signal of S_2^- in the pigments is observed only at a low temperature.[11] By using a standard of calibration, the absolute concentration of a radical can be determined.

Three studies related to the EPR determination of the concentration of S_3^- in the blue ultramarine pigments have already been published,[12−14] but neither the experimental procedure nor the preparation of the EPR samples was described. In 1968, Böttcher et al.[12] used pyrolyzed cellulose as a secondary quantitative standard (its concentration is determined by comparison with $CuSO_4 \cdot 5H_2O$) and found 8×10^{20} spins/g, that is, 0.67 spin (S_3^-)/cage. No estimation of uncertainty was given. Hofmann[13] investigated five different blue ultramarine samples by using a coal standard containing 3×10^{17} spins/g. The five results are 12.6×10^{20}, 11.80×10^{20}, 11.40×10^{20}, 9.21×10^{20}, and 8.50×10^{20}, that is, 1.19, 1.09, 1.04, 0.80, and 0.72 spins/cage, respectively (relative uncertainty, 10−20%). It is difficult to consider these results[13] reliable due to the following reasons. (1) Three of these results are at the limit of the maximum theoretical concentration of 1 S_3^-/cage. This is consistent with the uncertainty but rather hard to believe. (2) The range covered by the values is very broad. This is possible if the samples are very different, but these differences might have been correlated with another characteristic of the samples. Wieckowski[14] was mainly concerned with the profile of the EPR signal and the distribution of S_3^- over the investigated sample, which apparently was rather impure. (3) Furthermore, the investigated sample displayed a narrow EPR line (10 G at room temperature) which has never been observed by the present authors in blue ultramarine pigments. The investigated sample displayed a content lower than 1 S_3^-/β cage.

It is obvious that the determination of the absolute concentration of S_3^- per β cage in blue ultramarine is very important for the understanding of the various characteristics of these pigments. In the first part of this paper, a quantitative EPR experiment is described and aims at determining the absolute concentration of S_3^- in samples of blue ultramarine. The results will be compared with those given by a relative scale (EPR index), previously proposed,[15] which allows an easy comparison of the concentration of S_3^- in samples of blue ultramarine pigments.

The first part of this paper will show that less than half of the β cages are occupied by S_3^-. The second part of this paper will show that the concentrations of S_3^- or S_2^- can be strongly increased by heating the blue pigment under a dynamic vacuum, which implies that β cages contain sulfur species which can be transformed into S_3^- or S_2^-.

Part I: Determination of the Absolute Concentration of S_3^- in Blue Ultramarine Pigments by EPR Experiments

Quantitative EPR measurements are possible by using a standard of calibration. The method is based on a simple principle: the number of absorption centers in a medium is proportional to the amount of energy absorbed in that medium which is proportional to the area of the absorption EPR signal.[16] The comparison method is commonly used: the factor of proportionality between the EPR area and the number of spins is first determined for a standard sample, the spin concentration of which is accurately known. Then, the spin concentration of an unknown sample can be calculated from the area of its EPR signal recorded in exactly the same experimental conditions that were used for the standard sample. The method is based on a simple principle, but the experiments require many conditions to be fulfilled to get a reliable and accurate result.[17−20]

We have chosen $CuSO_4 \cdot 5H_2O$ as a standard and a ruby crystal as an inner standard. The choice of $CuSO_4 \cdot 5H_2O$ and of the ruby is explained below.

A. Choice of the Standard

The first step of the calibration is the choice of the standard. It should have physical and paramagnetic charac-

(9) Clark, R. J. H.; Franks, M. L. *Chem. Phys. Lett.* **1975**, *34*, 69.
(10) Clark, R. J. H.; Dines, T. J.; Kurmoo, M. *Inorg. Chem.* **1983**, *22*, 2766.
(11) Gobeltz, N.; Demortier, A.; Lelieur, J. P.; Lorriaux, A.; Duhayon, C. *New J. Chem*. **1996**, *20*, 19.
(12) Böttcher, R.; Wartewig, A.; Windsch, W.; Schunke, A. *Z. Naturforsch*. **1968**, *23*, 1766.
(13) Hofmann, U.; Herzenstiel, E.; Schönemann, E.; Schwarz, K. H. *Z. Anorg. Allg. Chem*. **1969**, *369*, 119.
(14) Wieckowski, A. *Phys. Status Solidi* **1970**, *42*, 125.
(15) Gobeltz, N.; Demortier, A.; Lelieur, J. P.; Duhayon, C. *J. Chem. Soc., Faraday Trans*. **1998**, *94*, 677.
(16) Poole, C. P. *Electron Spin Resonance*, 2nd ed.; Wiley: New York, 1982.
(17) Chang, T.-T. *Magn. Reson. Rev*. **1984**, *9*, 65.
(18) Yordanov, N. D. *Appl. Magn. Reson*. **1994**, *6*, 241.
(19) Dyrek, K.; Rokosz, A.; Madej, A. *Appl. Magn. Reson*. **1994**, *6*, 309.
(20) Eaton, S. S.; Eaton, G. R. *Bull. Magn. Reson*. **1980**, *1*, 130.

teristics similar to those of the unknown sample. These requirements have been listed in other publications[17,19] and will not be detailed here. As for the ultramarine pigments, neither a sample of pigment containing an accurately known concentration of S_3^- nor a NaS_3 solid exists. The concentration of S_3^- has already been determined but in nonaqueous solutions.[21] Therefore, other standards without S_3^- have to be used. We have chosen $CuSO_4 \cdot 5H_2O$ as a standard of calibration for several reasons. This compound is commercially available in powder (i.e., the same solid form as the ultramarine pigments) in a high-purity grade (99.999%, Aldrich), and is stable over a long period of time. Its spin concentration is easy to determine, as it contains 1 spin/molecule. It can be weighed with a high accuracy, and mixtures of $CuSO_4 \cdot 5H_2O$ and K_2SO_4 (99.99% Aldrich), which do not contain any paramagnetic species,[19] can easily be prepared to obtain a range of various spin concentrations, including the concentration of S_3^- in the ultramarine pigments. Hence, this compound is a convenient standard for the determination of the absolute concentration of S_3^- in the ultramarine pigments. However, the pentahydrated copper sulfate is not a perfect standard, because its EPR signal is anisotropic and wide,[17,19] whereas the EPR signal of S_3^- in the pigments is isotropic and rather narrow ($\Delta H_{pp} \approx 25$ G). Despite all these aspects, it is the best available standard at the moment. The EPR characteristics of the trihydrated vanadyl sulfate $VOSO_4 \cdot 3H_2O$ are similar to those of $CuSO_4 \cdot 5H_2O$.[19] We used it to check our calibration data.

The water content of the vanadyl sulfate and of the copper sulfate has been measured following the Karl Fisher method. The vanadyl sulfate contains 3.0 H_2O/molecule, and the copper sulfate contains 4.7 H_2O/molecule. These results have been taken into account in our calculations.

B. Inner Standard

To determine the spin concentration of an unknown sample, two methods are commonly used. The first consists of placing both the unknown sample and the standard sample in the cavity of the spectrometer and recording their EPR signal at the same time. In the second, we place the samples successively in the cavity, and we record one spectrum for each sample. The first method requires a double cavity, which was not available to us; therefore, we used the second method. The following disadvantage to this substitution method was found. A variation of sensibility takes place because of variations in the quality factor Q. This is due to differences in dielectric properties beween the unknown sample and the standard.[22] The Q factor decreases with increasing dielectric susceptibility of the investigated sample.[19] To correct the variations of the signal due to changes in the Q factor, we have chosen a ruby crystal as an inner standard. Hence, the area of the signal of the samples is normalized to the area of one of the lines of the ruby EPR signal, as described in the following section.

C. Experimental Section

The spectra have been recorded at room temperature with an ESP300 BRUKER spectrometer (X band) and a TE102 rectangular cavity.

The ruby crystal was embedded in molten paraffin at the bottom of a quartz (suprasil quality) tube (i.d., 6 mm). After solidification, the paraffin formed a concave surface. This tube was placed in the cavity of the spectrometer in such a way that the ruby was located just below the center of the cavity. The angular orientation of the crystal can be changed and controlled by the rotation of the quartz tube around its axis. This angular orientation has been chosen so that the lines of Cr^{3+} in the ruby will not overlap the signal of either Cu^{2+} (Figure 3a,b) or S_3^- (Figure 3c); otherwise, the area of these signals would be enhanced by the contribution of the Cr^{3+} lines.

A height of 1−2 mm of either ultramarine pigment or standard is placed in a flat bottom quartz (suprasil quality) tube (e.d., 5 mm; i.d., 4 mm) and accurately weighed. Along this height of powder, the irradiation of the powder in the spectrometer cavity can be considered as a constant. Depending on the sample, a 1−2 mm height corresponds to a mass of about 10−30 mg of powder.

The tube containing either the copper sulfate or the ultramarine pigment is placedinside the tube containing the ruby, which was previously placed in the cavity and kept in the same position. Whereas the ruby is located just below the center of the cavity, the powder sample is located at the center of the cavity, that is, where the microwave irradiation is maximum. The bottom of the sample tube lies on the paraffin upper surface; therefore, the location of the tube, as well as the irradiation of the sample, is reproducible, because the powder height can be considered a constant.[23]

The spectrum of the ruby is first recorded on a restricted magnetic field sweep width to get the line of Cr^{3+} located at $g = 1.278$. The spectrum of the sample (standard or pigment) is then recorded with the same conditions, except for the receiver gain and the sweep width. In both cases, the sweep width is broad enough to get the whole signal in each spectrum, as shown in Figure 3. The area of the ruby line and the Cu^{2+} or S_3^- signal are calculated by double numeric integration and normalized to the sweep width and receiver gain. The area of the S_3^- or Cu^{2+} signal is then normalized to the ruby area in order to eliminate the influence of the variation of the Q cavity factor. The area is also normalized to the weight of powder introduced in the tube. The value obtained is the normalized area of S_3^- or Cu^{2+} EPR signal per gram of sample.

D. Results

Samples of various concentrations in $CuSO_4 \cdot 4.7H_2O$ have been prepared by mixing the copper sulfate with the K_2SO_4 used as a diamagnetic matrix.[19] The concentrations of these samples are as follows: 153.4×10^{19}, 102.2×10^{19}, 76.7×10^{19}, 51.1×10^{19}, 10.2×10^{19}, and 5.1×10^{19} spins/g. Seventeen sample tubes were prepared. The spectrum of each one was recorded twice to obtain 34 points. The second spectrum of each sample was recorded after removing the tube from the cavity and replacing it inside. The data obtained, given in Figure 4, indicate a good correlation between the area and the Cu^{2+} concentration. The fit of the data points to a linear variation gives the equation area/g $= 1.148 + (9.4530 \times 10^{-19}) \times C$, where C is the concentration in spins per gram. The correlation coefficient r is equal to 0.9988.

(21) Pinon, V.; Levillain, E.; Lelieur, J. P. *J. Magn. Reson*. **1992**, *96*, 31.
(22) Singer, L. S. *J. Appl. Phys.* **1959**, *30*, 1463.
(23) Yordanov, N. D.; Genova, B. *Anal. Chim. Acta* **1997**, *353*, 99.

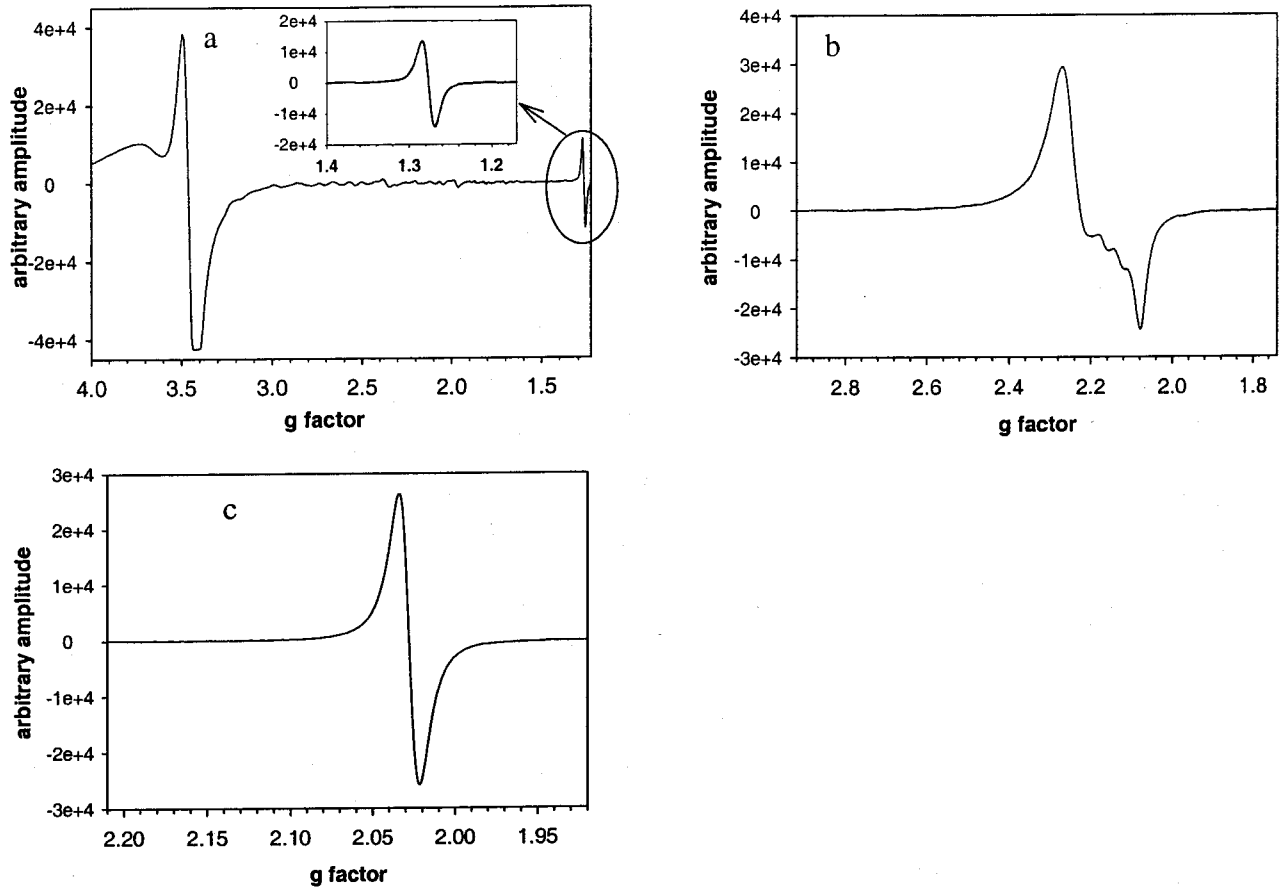

Figure 3. (a) EPR spectrum of the ruby crystal embedded in the paraffin, without copper sulfate or ultramarine pigment. The circled part of the spectrum displays the line of the ruby signal ($g = 1.278$) used to normalize the signal of the copper sulfate, vanadyl sulfate, or ultramarine pigments. (b) EPR spectrum of $CuSO_4 \cdot 4.7H_2O$ with the sample placed in the tube containing the ruby crystal: no contribution of the ruby is observed. (c) EPR spectrum of a blue ultramarine sample placed in the tube containing the ruby crystal: no overlapping of the lines of the S_3^- and of the ruby is observed.

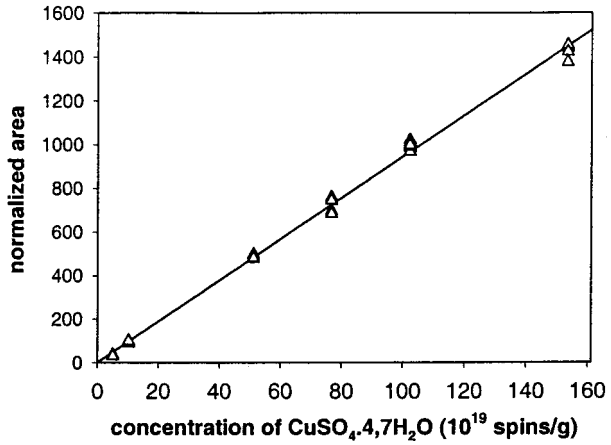

Figure 4. Correlation between the area of the EPR signal of Cu^{2+} and the spin concentration in the standard mixtures of $CuSO_4 \cdot 4.7H_2O$ and $K_2SO_4 \cdot 3H_2O$ (triangles, experimental points; line, regression line).

To check this result, we have determined the concentration of a sample of $VOSO_4 \cdot 3H_2O$, which is also a standard of calibration. Three samples of pure $VOSO_4 \cdot 3H_2O$ were prepared, and their spectra were recorded with the method described above. The average concentration calculated with the calibration line is $(264.7 \pm 3.5) \times 10^{19}$ spins/g, whereas the theoretical concentration is 277.4×10^{19} spins/g. To estimate the error in the spin concentration calculated by using the regression line, we used an adequate statistic formula.[24] This error depends not only on the quality of the calibration line (dispersion of the data, number of experimental measurements) but also on the number of points for the unknown samples and on the location of the experimental value of the unknown sample in the calibration interval ($153.4-5.1 \times 10^{19}$ spins/g).

The calculated error does not take into account the following fact that during the preparation of the EPR tube, despite all the care taken, some particles may remain stuck on the inner surface of the quartz tube. Consequently, the powder weighed is not entirely located in the bottom of the tube. This would lead to underestimating the spin concentration and may explain the difference between the theoretical concentration and our result concerning the spin concentration in $VOSO_4 \cdot 3H_2O$.

Without normalizing the area of the samples to the area of EPR signal of the ruby crystal, we can obtain a calibration line. The correlation coefficient is $r = 0.9986$, and the equation is area/g $= 1.227 + (1.9421 \times 10^{-19}) \times C$ spins/g. The concentration of vanadyl sulfate calculated with this regression line is 223.5×10^{19} spins/g. This result is not very satisfactory, since the theoretical concentration is 277.4×10^{19} spins/g. These results show the importance of

(24) Miller, J. C.; Miller, J. N., *Statistics for Analytical Chemistry;* Wiley: New York, 1984; p 94.

Table 1. Results of the Calculation of the Absolute Concentration of S_3^- in Three Samples of Blue Ultramarine Pigments Compared with the Relative Concentration (EPR Index)[a]

sample	n°1	n°2	n°3
10^{19} spins/g	44.3 ± 2.0	53.5 ± 2.3	10.1 ± 2.5
spins/cage	0.36 ± 0.04	0.43 ± 0.05	0.08 ± 0.05
EPR index	100 ± 3	131 ± 4	23 ± 1

[a] The concentration in spins per cage has been calculated by estimating the molecular weight at 971.2 g/mol which corresponds to the formula $Na_6(Al_6Si_6O_{24})\cdot NaS_3$. It is difficult to know the exact molecular weight, considering that less than 0.5 of the S_3^- are inserted per cage, and that S_2^- ions and water are also inserted but in an unknown concentration.

the inner standard, especially if one wants to determine the absolute concentration of samples of various types.

Three samples of blue ultramarine pigments have been investigated through the same procedure as the one used for the copper and vanadyl sulfates. The samples were selected after investigation by Raman and EPR (EPR index) spectroscopies: the first and second samples contain a low concentration of S_2^- and a high concentration of S_3^-. The third sample contains a low concentration of both S_3^- and S_2^-. The first sample is the reference blue pigment used in the determination of the EPR index and is a highly colored industrial pigment. The results are given in Table 1.

The concentrations of the investigated samples calculated from the equation of the calibration line are expressed in spins per gram. To convert these values in spins per cage, we need to know the molecular weight of the pigment. However, this molecular weight depends on the content of the β cages. Hence, it is impossible to determine the exact molecular weight of each sample of blue ultramarine. We have estimated the molecular weight to be 971.2 g/mol, which corresponds to the formula $Na_6(Al_6Si_6O_{24})\cdot NaS_3$. The concentration of S_3^- calculated for the first two samples is somewhat lower than 0.5. We may consider that this molecular weight is underestimated, because the pigment also contains the yellow chromophore, and therefore, the concentration of S_3^- may also be underestimated. The upper limit of the molecular weight corresponds to 1 S_3^-/cage (1090.4 g/mol). If we used this value, we would find 0.40 spin/cage for the first sample instead of 0.36 spin/cage. This result shows that the variations of the molecular weight of the ultramarine pigment do not lead to important variations of the occupancy of the sodalite cages by S_3^-.

The absolute concentration obtained by the calibration line is compared (Table 1) with the relative concentration of S_3^- (EPR index determined with an error of $\pm 3\%$). The EPR index and the absolute concentration are proportional within the limit of uncertainty (Table 1). This is an indication of the validity of the results.

E. Discussion

The maximum value of the absolute concentration of S_3^- in our samples is equal to $53.5 \times 10^{19} \pm 1.3\%$ spins/g, that is, approximately 0.43 S_3^-/cage. This result indicates that less than half of the cages are occupied by a blue chromophore, and that a higher occupancy can be expected.

It is now established that at least half of the sodalite cages do not contain any S_3^- chromophore. The cages which do not contain any S_3^- can contain the yellow chromophore. So far, it is impossible to determine the absolute concentration of S_2^-. This is why we cannot know if all of the cages contain either S_3^- or S_2^-. However, it is usually claimed,[10] on the basis of electronic and Raman data, that S_3^- is the predominant chromophore in blue pigments. As a consequence, a fraction of β cages could not be occupied by either S_3^- or S_2^-. In the second part of this paper, we give evidence that the concentration of S_3^- and S_2^- can be simultaneously increased, and that, consequently, there is another sulfur species inserted in the β cages.

Part II: Evidence of a Supply of Reduced Sulfur Species Which Can Be Transformed into Chromophores

A. Experimental Section

Samples of an industrial blue pigment, very similar to the n°1 pigment of Table 1, were heated under a dynamic vacuum according to the following procedure. Two grams of pigment was introduced into a Pyrex or quartz tube. The tube was placed in a tubular oven and connected to a vacuum line. The tube was heated for 5 h at a given temperature (from 150 to 700 °C) while being pumped under a vacuum (10^{-5} mmHg). The tube was cooled to room temperature under a vacuum. Each heating under a vacuum was naturally performed on a new unheated sample.

After this treatment, the EPR and the Raman signals of the modified pigment were recorded. The method of determination of the EPR index is detailed in another article[15] and, therefore, will not be explained in detail here.

Raman spectra were recorded with an RT30 Dilor spectrometer at room temperature. The samples (powder) were pressed into a rotatable die, and the excitation power was kept lower than 75 mW to minimize the risk of thermal decomposition of the samples at the beam focus. The backscattered light was collected. We have chosen the 457.9 nm excitation line, so we could observe S_3^- and S_2^- simultaneously. At this wavelength, the vibration band of S_2^- (590 cm^{-1}) is enhanced by the resonance effect, because the yellow chromophore absorbs at ca. 420 nm, whereas the ν_1 band (545 cm^{-1}) of S_3^- absorbs at ca. 620 nm and is not enhanced by the resonance effect, but can still be easily observed.

For a given excitation line, the ratio of the intensity of the 590 cm^{-1} band to that of the 545 cm^{-1} band is proportional to $[S_2^-]/[S_3^-]$. We can write

$$I(590\ \text{cm}^{-1})/I(545\ \text{cm}^{-1}) = \alpha \times [S_2^-]/[S_3^-] \qquad (1)$$

where α is a constant for a given excitation line.

The EPR index is the relative concentration of S_3^-

$$\text{EPR index} = \lambda \times [S_3^-] \qquad (2)$$

where λ is a constant, since the same reference pigment has been used to determine this index.

Consequently, the relative concentration of the yellow chromophore can be deduced by the following equation

$$\beta \times [S_2^-] = \text{EPR index} \times [I(590\ \text{cm}^{-1})/I(545\ \text{cm}^{-1})] \qquad (3)$$

where β is a constant (equal to the product of $\alpha\lambda$). This means that the EPR and Raman spectra can be used to determine a quantity

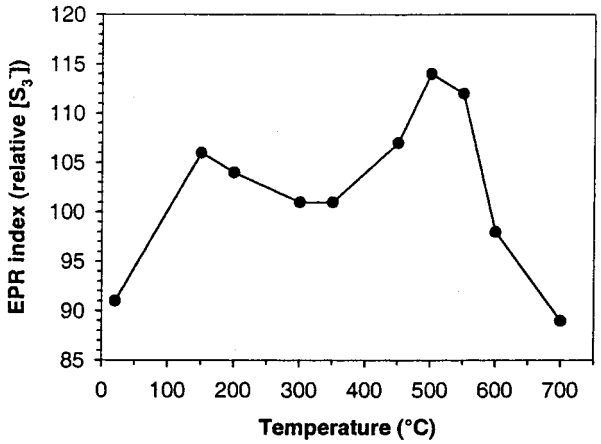

Figure 5. Variation of the EPR index (relative concentration of S_3^-) of a blue pigment as a function of the temperature of heating under a dynamic vacuum. An increase of the concentration of the blue chromophore S_3^- is observed; except for the sample heated at 700 °C, all other samples display an increase of the S_3^- concentration compared to that of the unheated sample. The uncertainty on the EPR index is estimated to ±3%.

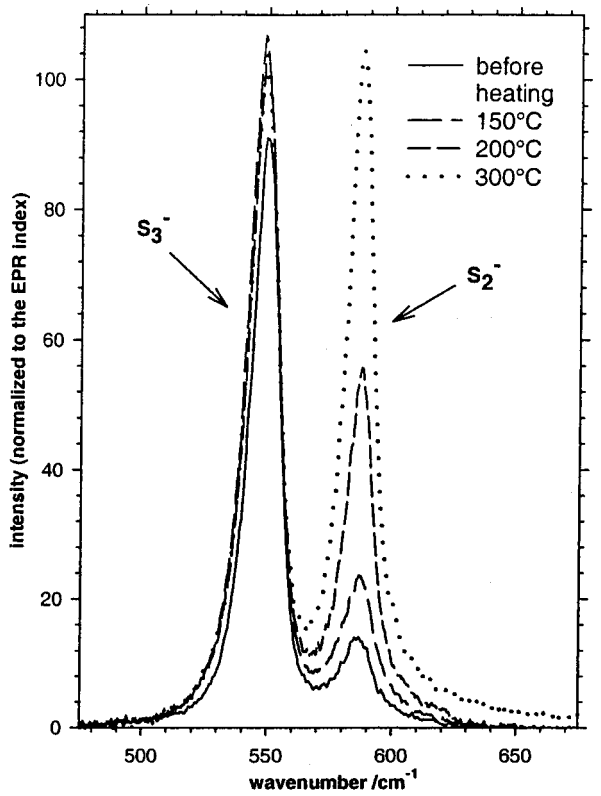

Figure 6. Variation of the Raman spectra (λ_{exc} = 457.9 nm) of the blue pigments after heating for 5 h at various temperatures under a dynamic vacuum. The intensity is normalized to the concentration of the blue chromophore (EPR index): the value of the EPR index has been given to the intensity of the 545 cm^{-1} band of S_3^-. The intensity of both S_3^- and S_2^- bands is increased after heating under a dynamic vacuum.

proportional to [S_2^-], for example, the concentration of S_2^- on an arbitrary scale.

B. Results and Discussion

The variation of the EPR index indicates that the concentration of S_3^- is higher after being heated under a dynamic vacuum (Figure 5), except for the 700 °C heating experiment. The observed increase of the concentration of S_3^- is much higher than the uncertainty of the experiments. At 500 °C, the EPR index is increased from 91 to 114, which represents ca. 20%. The Raman investigation shows that the relative concentration ratio of S_2^-/S_3^- also increases with the temperature of heating under a dynamic vacuum (Figure 6). The EPR and Raman data can be used following eq 3 to obtain the relative concentration of S_2^- (Figure 7) versus the temperature of heating: it is shown that the concentration of S_2^- is increased, no matter what the heating temperature was (up to 700 °C).

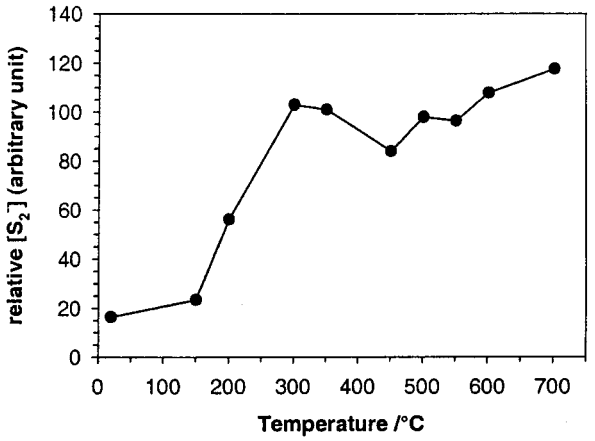

Figure 7. Variation of the relative concentration of S_2^- (calculated from eq 3) as a function of the temperature of heating under a dynamic vacuum of the blue pigment. A strong increase in the concentration of the yellow chromophore S_2^- is observed. After heating at 700 °C under a dynamic vacuum, the concentration of S_2^- is more than 5 times higher.

Therefore, the results reported in Figures 5−7 show that after heating under a dynamic vacuum, the concentration of both S_3^- and S_2^- is increased. Hence, we note an increase of the total number of sulfur atoms involved in the chromophores of the pigment. Obviously, this implies that sulfur species are being transformed into chromophores during the experiment of heating under a vacuum. This species is not observed in either Raman or IR, and therefore, it has no vibration mode. It is not observed in EPR. Even at 4.2 K, there is no indication that this species is paramagnetic. We suggest identification of this sulfur species with the sulfide S^{2-}. The double-negative charge of the sulfide ion must be balanced by two sodium cations which can be in two neighboring sodalite cages, following the usual assertions. An EPR index of 91 before heating (Figure 5) corresponds to 32% of the β cages being occupied by S_3^-. The increase of the EPR index from 91 up to 114 (after heating at 500 °C, Figure 5) corresponds to an increase from 32 to 40% of the β cage occupancy by S_3^-. This increase should originate from 24% of the β cages being occupied by S^{2-}. If the double-negative charge of S^{2-} is balanced by two sodium cations in two neighboring cages, this implies that 48% of the β cages have been involved with S^{2-}. Therefore, before heating, 80% of the β cages were involved by the insertion of either S_3^- or S^{2-}. These estimations can be considered as realistic, because the yellow chromophore has not been taken into account.

Two points have to be discussed: (1) the origin of the "hidden" sulfur species leading to the chromophores and (2)

the mechanism of these transformations. What could be the origin of these sulfur species? It is now well established[25] that polysulfides originate from the reaction of sulfur with sodium carbonate, which leads to the formation of S_4^{2-} at a temperature of ca. 260 °C. When the temperature of the reaction mixture is increased, S_4^{2-} is disproportionated into more-reduced and more-oxidized species. The most-reduced form is obviously S^{2-}, while the most-oxidized form is sulfur. When the three-dimensional structure of sodalite is formed in the synthesis medium, chromophores (S_3^-, S_2^-) are encapsulated in the β cages,[26] but other species present at these temperatures can also be inserted. This enables us to understand the presence of S^{2-} in the β cages. At the temperatures where the structure is formed (ca. 600−700 °C), the vapor phase of sulfur is composed of small molecules such as S_2, S_3, or S_4.[27,28] If these species had been inserted in the β cages, their Raman spectra would have been observed, for instance, S_4, which seems to be observed in the pink ultramarine pigments.[8] There is no indication of a possible insertion of these species in the blue pigments. Therefore, we suggest that the hidden sulfur species is S^{2-}, which acts as the sulfur supply in the formation of chromophores when the pigment is heated under a dynamic vacuum.

A second point needs to be discussed, that is, the mechanism of the transformation of S^{2-} into the chromophores. One might be surprised to find that a pigment synthesized at 700−800 °C can be significantly modified later on by heating under a dynamic vacuum. We need to emphasize the fact that after synthesis the pigments are washed with water. After drying, their water content is determined to be equal to 1−2 wt %. A water content of 2% corresponds to about 1 water molecule for 2 β cages. We have observed[29] that the modifications of the pigment are not identical after being heated at a given temperature under a static vacuum or under a dynamic vacuum. It has also been observed that, after heating under a static vacuum, the modifications of the pigment depend on the filling factor of the cell. These observations indicate that the modifications of the pigments are induced by gaseous species (such as SO_2 or H_2S) resulting from the reaction of water with the species inserted in the β cages. The presence of these gaseous species has been demonstrated by the IR study of the gas evolved during heating under a vacuum. Part of the water content of the pigment can be evacuated in the form of water, but a part can react with species inserted in the cages, leading to H_2S and SO_2, which can either be evacuated far from the pigment or react with it. The observed modifications of the pigment are the overall result of several competing mechanisms. A detailed interpretation of Figures 5−7 is presently not available.

Conclusion

The experiments reported in this paper show that in a typical highly colored blue ultramarine pigment, less than half of the cages are occupied by S_3^-. These experiments have also shown that the concentration of S_3^- and S_2^- can be significantly increased by heating under a dynamic vacuum, which implies that hidden sulfur species can be transformed into chromophores. We suggest that these species are S^{2-} anions, resulting from the disproportionation of polysulfides at the high temperatures of the synthesis, and that the increase of the concentration of the chromophore is induced by gaseous molecules resulting from the reaction of a part of the water content of the pigment with the species inserted in the cages.

Acknowledgment. The authors thank the Holliday Pigments Company for providing samples and Dr. A. Lorriaux and Dr. L. Boussekey for their assistance in the Raman data collection.

IC010822C

(25) Gobeltz, N.; Demortier, A.; Lelieur, J. P. *Inorg. Chem.* **1998**, *37*, 136.
(26) Gobeltz, N.; Demortier, A.; Lelieur, J. P.; Duhayon, C. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2257.
(27) Lenain, P.; Picquenard, E.; Corset, J.; Jensen, D.; Steudel, R. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 859.
(28) Boumedien, M. S.; Corset, J.; Picquenard, E. *J. Raman Spectrosc.* **1999**, *30*, 463.
(29) Gobeltz, N.; Demortier, A.; Lelieur, J. P.; Duhayon, C, unpublished results.