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- [2] S.B. Hawthorne, *Anal. Chem.* **1990**, *62*, 633A.
 [3] J.W. King, *J. Chromatogr. Sci.* **1989**, *27*, 355.
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 [5] R.W. Vannoort, J.P. Chervet, H. Lingenman, G.J. Dejong, U.A. Brinkman, *J. Chromatogr.* **1990**, *505*, 45.
 [6] K.G. Furton and J. Rein, *Anal. Chim. Acta* **1990**, *237*, 99.
 [7] J.D. Pinkston, T.E. Delaney, D.J. Bowling, T.L. Chester, *High Resolut. Chromatogr.* **1991**, *14*, 401.
 [8] E. Stahl, *J. Chromatogr.* **1977**, *142*, 15.
 [9] S.M. Fields, K. Grolimund, *J. High Resolut. Chromatogr.* **1988**, *727*, 11.
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 [11] O. Gyllenhaal, J. Vessman, *J. Chromatogr.* **1990**, *516*, 415.
 [12] T.L. Chester, D.P. Innis, *J. High Resolut. Chromatogr.* **1986**, *9*, 178.
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 [16] J.L. Veuthey, W. Haerdi, *J. Chromatogr.* **1990**, *515*, 385.
 [17] R.M. Smith, M. Sanagi, *J. Chromatogr.* **1989**, *483*, 51.
 [18] R.M. Smith, M. Sanagi, *J. Chromatogr.* **1989**, *481*, 63.
 [19] D.W. Roberts, I.D. Wilson, *Methodol. Surv. Biochem. Anal.* **1990**, *257*.
 [20] W. Steuer, J. Baumann, F. Erni, *J. Chromatogr.* **1990**, *500*, 469.
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 [24] S.H.Y. Wong, *Clin. Chem.* **1989**, *35*, 1293.
 [25] R.L. Eatherton, M.A. Morissey, H.H. Hill, *Anal. Chem.* **1988**, *60*, 2240.
 [26] L. Karlsson, L. Mathiasson, J. Akesson, J. Jonsson, *J. Chromatogr.* **1991**, *557*, 99.
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 [28] B.E. Richter, D.E. Knowles, M.R. Andersen, N.L. Porter, E.R. Campbell, *J. High Resolut. Chromatogr.* **1988**, *11*, 29.
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 [30] B.E. Berg, T. Greibrokk, *J. High Resolut. Chromatogr.* **1989**, *12*, 322.
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Renata Reisfeld^{a)}, Valery Chernyak^{a)}, and Christian K. Jørgensen^{b)}*

Abstract. Malachite Green (MG) incorporated in glass appears in four forms. In acidic glasses, yellow H(MG)²⁺ protonated dications; the green monocation MG⁺ in H₂O at pH 4 to 6; the colorless carbinol base HO(MG) at higher pH; and a new purple species in certain glasses prepared by mineral acid catalysis. Uniquely high luminescence yields indicate formation of chemical bonds between MG⁺ and the silicate groups, suggesting Lewis-acid behavior of three-coordinated carbon. Novel cascade emission is observed from the three first excited singlets S₁, S₂, and S₃. In sol-gel glasses, green MG⁺ bleaches reversibly under illumination.

Introduction

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A systematic study of absorption and in particular the novel emission spectra

showing high luminescence yields as a function of preparative procedure [2][3] give the motivation to attempt a rationalization of the unusual spectroscopy based on a general distinction between the coordination numbers $N=3$ and $N=4$ of carbon in aromatic molecules and ions.

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The most frequent coordination number of non-aromatic C-atom is 4. Planar aliphatic compounds with $N=3$ such as formate HCO₂⁻, aqueous carbonic acid (HO)₂CO and bicarbonate HOCO₂⁻ do not usually absorb in the visible or near UV.

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Introduction

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showing high luminescence yields as a function of preparative procedure [2][3] give the motivation to attempt a rationalization of the unusual spectroscopy based on a general distinction between the coordination numbers $N=3$ and $N=4$ of carbon in aromatic molecules and ions.

It is especially appealing to study the monocationic form of Malachite Green MG⁺ ([PhC(C₆H₄NMe₂)₃]⁺) and its proto-

nated form in gel glasses [3], in which the luminescent ions are situated in a small isolated cavity. Recently, a gel glass composed of SiO₂ and ZrO₂ [1] containing MG⁺ was shown to become reversibly transparent to incident energies of microjoules with a recovery time of picoseconds.

In (MG) the colorless form is attributed here to the four-coordinated C-atom in the carbinol HO(MG) and the colored forms to three-coordinated C-atom in green MG⁺ and in the yellow protonated dication H(MG)²⁺. Our suggestions are based on the following consideration:

The most frequent coordination number of non-aromatic C-atom is 4. Planar aliphatic compounds with $N=3$ such as formate HCO₂⁻, aqueous carbonic acid (HO)₂CO and bicarbonate HOCO₂⁻ do not usually absorb in the visible or near UV.

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The situation is different in strongly conjugated compounds with which we are dealing here. In most of these conjugated systems the compounds having four coordinated C-atom are colorless, while those having three coordinated C-atom become strongly colored. Thus, triphenylcarbinol [4] HOCPH_3 reacts with strong acids to form the orange Ph_3C^+ of which salts with BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , and ClO_4^- can be isolated [5][6]. Also strongly alkaline solvents (e.g. NH_2^- in liquid ammonia) form red carbanions Ph_3C^- with $N=3$ contrary to the colorless molecules with $N=4$ Ph_3CH and Ph_3CCl .

The new aspect here is the effect of oxygen containing anions in adjacent sites for rearrangements of strongly colored ($N=3$) and related ($N=4$) aromatics. Many triphenylmethane colorants such as Crystal Violet (= Gentian Violet) $\text{C}[\text{C}_6\text{H}_4\text{NMe}_2]_3^+$ (in this note CV^+) with three, and Malachite Green $\text{PhC}[\text{C}_6\text{H}_4\text{NMe}_2]_2^+$ (in this note MG^+) with two *p*-(dimethylamino) substituents were studied (in Jerusalem) from the point of view of luminescence in highly viscous solvents, and in sol-gel prepared glasses [2][3]. These two colorants behave as immediately reversible pH indicators in aqueous acid, MG^+ forming yellow $\text{H}(\text{MG})^{2+}$ and Crystal Violet green $\text{H}(\text{CV})^{2+}$ and yellow $\text{H}_2(\text{CV})^{3+}$ when protonating the $N=3$ N-atoms to $N=4$ (the authors do not know to what extent this protonation may modify the coplanarity of the 11 nuclei in $\text{C}_6\text{H}_4\text{N}$). The strongly colored cations all have $N=3$ of the central C-atom coordinated to the three C_6 hexagons. At a given pH, however, slow equilibria are established between colorless carbinols $\text{H}_2\text{O}(\text{MG})$ and protonated $(\text{H}_2\text{O})\text{MG}^+$ studied extensively [7–10], also for differing MG substituted on several positions on the remaining Ph ring.

In view of the strong (and quite broad) absorption bands of the $N=3$ species, it is not easy to be certain that adjacent, weaker bands (a band 30 times weaker than the 620-nm band of green MG^+ would be as intense per mol as the 526-nm band of permanganate) do not occur in the $N=4$ hydroxy species (although aliphatic $\text{Me}_3\text{COH}_2^+$ and MeOH_2^+ are strictly colorless; these 'aqua ions' are only slightly more acidic than H_3O^+). Anyhow, the slow rearrangements between $N=3$ and 4 make the intensities of the absorption maxima of $N=3$ apparently less reproducible [11][12].

Förster and Hoffman [13] found near-IR luminescence of CV^+ to be almost imperceptible in solvents of low viscosity, but the yield increases almost proportionally to the square root of viscosity. Analogous results were reported [14] for red

emission of MG^+ , although with yields remaining below a few percent. The rapid nonradiative relaxation in H_2O of the emitting state with lifetime [15] of only 3 ps as compared with the radiative lifetime of few ns, is connected with the crossing [1][13–17] of two multidimensional Born-Oppenheimer potential surfaces. Here, a set of internuclear distances is highly modified, for instance by a strong relative rotation of the Ph rings, allowing the ground state and the luminescent state to cross or to approach closely.

Experimental Results on the Ground-state

The sol-gel glasses with Malachite Green were prepared from $(\text{MeO})_4\text{Si}$ (TMOS), containing varying concentrations of H_2O and MeOH, and using the following catalysts: methacrylic acid, AcOH, HF, H_3PO_4 , HCl, HNO_3 , or H_2SO_4 , or dilute NaOH and one experiment without any catalyst. The detailed ratio between components and the serial of preparation may be found in [2]. The temperature of drying varied between 50 and 100°. Glasses prepared using methacrylic

acid, AcOH, HF, or NaOH as catalysts showed the blue green color of monocation MG^+ (predominant at pH 4 to 6 in aqueous solutions) with absorption peaks close to 615, 420, and 312 nm and emission typically at 650 nm (Fig. 1). It turns out that these transitions vary only within the limits 620.7 ± 4.4 , 425.6 ± 2.2 , and 315 ± 1.5 nm in ten differing solvents and polymers (Table).

When the sol-gel glass is prepared at very strong acidic conditions, or impregnated by a strong acid, only the yellow $\text{H}(\text{MG})^{2+}$ is perceived. This has an absorption maximum [2] at 420–450 nm emitting around 570 nm.

A striking effect of ammonia on MG^+ is also presented in Fig. 1 where a glass prepared with molar ratios of TMOS/ H_2O /methacrylic acid of 1:16:10⁻³ and containing 7.4×10^{-6} M of the MG^+ oxalate, subsequently immersed in 0.5M aq. NH_3 (pH 11.5), decreases its absorption in the red to about a third, while the non-eluted MG^+ in the glass increases dramatically its quantum efficiency of 670 nm fluorescence from 0.003 to 0.2.

The explanation of this unexpected behavior may be that the NH_3 in solution reacts with the loosely bound MG^+ dis-

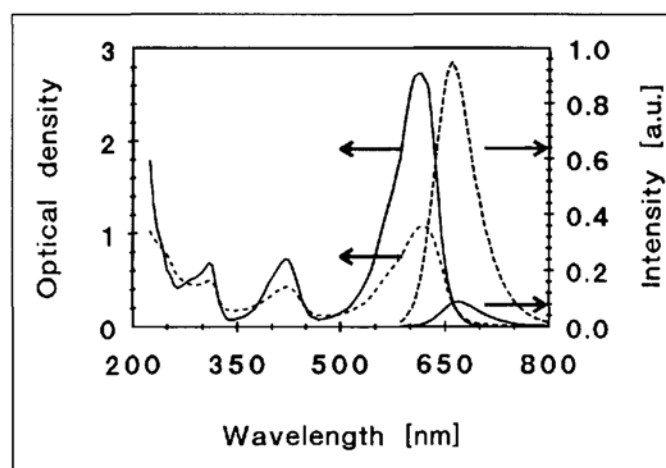


Fig. 1. Absorption and luminescence spectra of MG^+ in sol-gel bulk before (full lines) and after (dashed lines) immersion in 0.5M aq. ammonia for 24 h. The glass was prepared from molar ratios $(\text{MeO})_4\text{Si}$: 16 H_2O : 0.001 methacrylic acid, and originally containing $7.4 \mu\text{M}$ MG^+ oxalate. Both optical intensity and luminescence intensity are plotted vertically in arbitrary units.

Table. Absorption Peaks [nm] of Malachite Green Oxalate in Various Media

Media	S ₁	S ₂	S ₃
Sol-gel bulk	615	423	313
Tetra(methoxy)silane	619	422	313
H_2O	615	422	314
MeOH	617	424	314
EtOH	619	425	314
PrOH	620	425	–
CHCl_3	621	425	315
Poly(methyl methacrylate)	625	425	316
Glycerol	627	429	317
Polyvinyl alcohol	629	432	316

solved within the cavities (perhaps also forming HO(MG) to some extent). The remaining MG⁺ molecules become chemically bound to the silicate groups forming complexes of the type R₃C⁺OSi(O...)₃⁻.

When the sol-gel glass is impregnated at sufficiently low pH, only the yellow H(MG)²⁺ is perceived, having a band close to 430 nm (an extreme case being 450 nm, emitting around 570 nm). Out of 29 differing experimental conditions of MG-doped gel glasses, five [2] samples derived from very dilute HCl or H₃PO₄ (as hydrolysis and oligomerization catalyst) showed an atypical absorption band between 584 and 547 nm, they had been dried at 55° between 11 and 21 d. The lowest wavelength (547 nm) corresponding to raspberry color (580 nm corresponds to blue-violet) was observed in a sample, originally containing 0.008M H₃O⁺Cl⁻ and 3M (MeO)₄Si in H₂O (with no MeOH) which had then been heated 2 d to 100° after drying for 21 d at 55°. The absorption spectrum cannot be a superposition of bands of yellow H(MG)²⁺ and green MG⁺. If a novel photodecomposition process is excluded, such samples are likely to be ambiguous intermediate cases between direct coordination O₃SiO(MG) and a quite long distance between the closest group and the central C-atom of MG⁺.

Fig. 2 presents three typical absorption spectra of Malachite Green in sol-gel glass-

es prepared under different experimental conditions. Curve 1 is a spectrum of a standard MG⁺, curve 2 is the spectrum of a purple glass which was prepared with diluted H₃PO₄ as a catalyst, curve 3 has an absorption maximum at 450 nm, is the absorption spectrum of a glass prepared under strongly acid conditions with 0.1M H₂SO₄ in the starting solution, it is due to H(MG)²⁺. As stated above, the detailed preparation has been described [2] as well as generalities about such glasses [3].

Brønsted acidity involving a base B (with whatever charge), and its protonated form BH (with one charge more) has been studied in the case of Oxazine 170 [18][19]; and the highly luminescent 2,2'-bipyridyl-3,3'-diol [20] undergoing internal H-bonding and tautomeric proton mobility in various nonviscous solvents, in polymethylmethacrylate and sol-gel glasses [3].

Another way to explain the above behavior may also involve Lewis acidity [21] where a definite (possibly proton-free) Lewis acid forms a strong adduct with a base (with a reactive pair of electrons in the Lewis paradigm [24]). Contrary to the proton affinity of a base, which can be described accordingly to Brønsted by one pK value in a given solvent (which can be protonated) the affinity between a Lewis acid and a given base, can not generally be described by the sum of the logarithms of an acid and a base strength. A striking case

is B(OH)₃, showing strong affinity to some bases, allowing the coordination number *N* of boron to increase from 3 to 4. In H₂O B(OH)₄⁻ is formed [25] with an effective pK=9 of H₂O+B(OH)₃, and at higher borate concentrations, also B₃O₃(OH)₄⁻; and B₃O₃(OH)₅²⁻ and/or B₄O₄(OH)₆²⁻ known from crystalline borax. However, α,β-diols R(CH₂OH)₂ react quantitatively with B(OH)₃ to give *N*=4 bidentate [R(CH₂O)₂]₂B⁻ with so low a proton affinity that either R(CH₂OH)₂ or B(OH)₃ can be titrated as a strong Brønsted acid in presence of a large excess of the other reactant.

The coordination to boron has been shown in fluorescein (here flu⁰, existing as two tautomers in different solvents) can be [26] protonated to [H(flu)]⁺ at low pH (pK is 2.2) having a quite characteristic absorption spectrum. Molten boric acid (dehydrated to ca. B₁₁O₁₆(OH)) dissolves flu⁰, as a similar species, showing a highly unusual luminescence. At liquid air temperature, the first triplet state emits in the orange with a long lifetime. Warming up to room temperature, this emission is replaced by a greenish blue band, still with the observed lifetime of several (up to 20) s, at the same energy as the exceedingly rapid (10⁻⁸ s) emission. The phenomenon is called 'delayed fluorescence', the triplet state being (very slowly) thermally excited to the first excited singlet of flu⁰ bound to boric acid glass. In other situations, including sol-gel glass hosts [3][27] flu⁰ loses two protons (one derived from a carboxylic substituent) with pK=4.4 and 6.7 in aqueous solution [26] providing broad-band green emission (between the first excited singlet and the ground state) with quantum yield above 0.9.

It was noted above that the purple species of MG in glass (Fig. 2) may have direct, but perhaps highly asymmetric, CO-Si contacts. It was shown by Cigén [28] that ortho CH₃OC₆H₄C[C₆H₄NMe₂]₂⁺ reacts with borate (diols, and polyols, e.g. mannitol) with high affinity. However, this borate adduct [28] does not connect BO-C* to the central C*-atom, but to the MeO group, forming a six-membered ring OBOC₃. It is, of course, possible to imagine the carbinol adding *N*=3 boron. Bengtsson [10] discusses equilibria and kinetics of yellow [Gelb] G, considered by us as (HR)CR₂²⁺, blue B [CR₃⁺], colorless C [HOCR₃], and the two protonated S' [probably H₂OCR₃⁺] and S'' [conceivably H₂OC(RH)R₂²⁺, if not a tautomer], although his scheme on p.1138 ascribes one more positive charge to all five species. On the other hand, Cigén gives on p.1906 of our last reference [7] the same charges as we assume. Among the corollaries are that the individual concentrations [B]/[G] have the

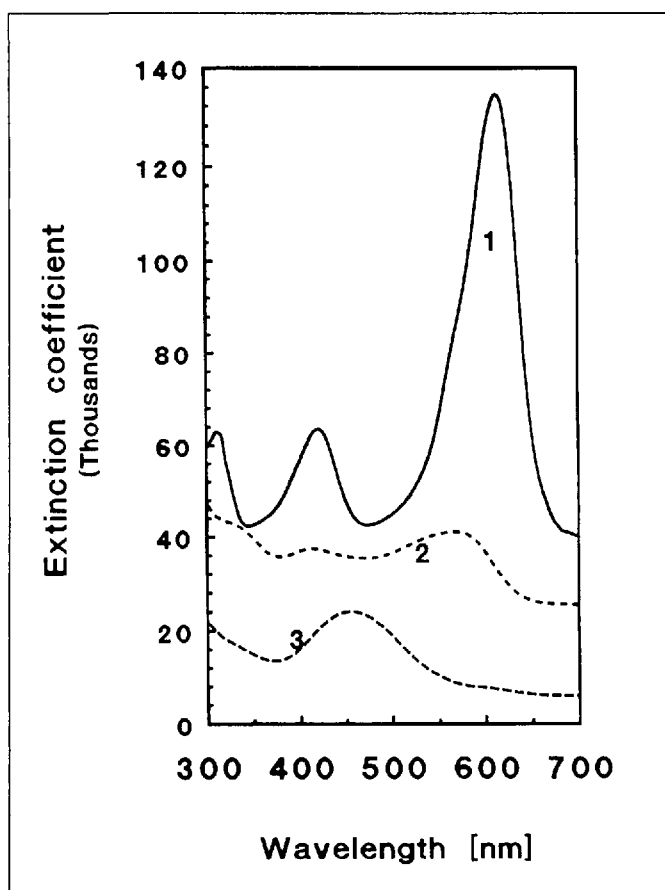


Fig. 2. Absorption spectra of three typical sol-gel glasses. 1: Like MG⁺ made from 1 (MeO)₄Si: 16 H₂O: 0.001 methacrylic acid and dried 10 d at 55°; 2: (purple species) made from 1 (MeO)₄Si: 8 H₂O: 11 MeOH: 0.002 H₃PO₄, dried 10 d at 25° and then 11 d at 55° (maximum: 552 nm [2]); 3: (like H(MG)²⁺) made from 1 (MeO)₄Si: 16 H₂O: 0.34 H₃PO₄, dried 4 d at 55°.

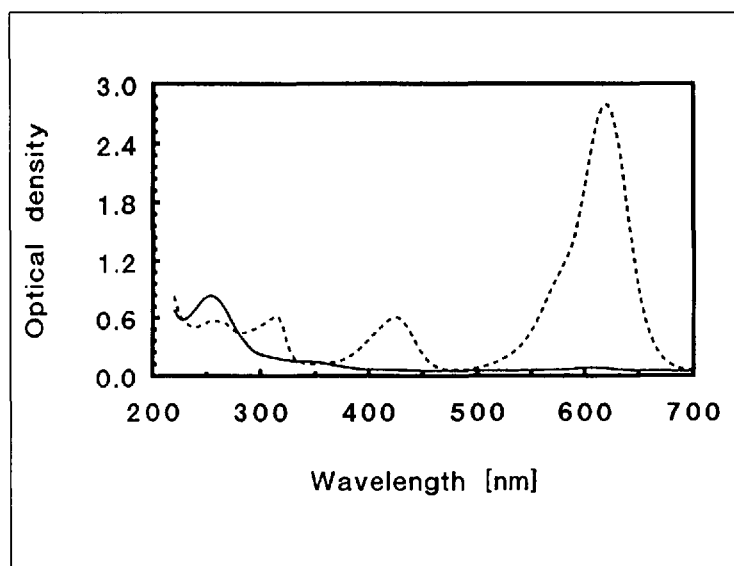


Fig. 3. Absorption spectra of 26 micromolar MG^+ oxalate in EtOH before (dashed line) and after (full line) solar irradiation for 3 d

ratio 0.6 at pH=1, 60 at pH=3, and 600 000 at pH=7, indicating $pK=1.2$ of the protonated G. The ratio $[B]/[S']$ called [10] $K_6=9$ shows that at any pH, a tenth of $[B] + [S']$ occurs at the hydrated cation of carbinol. The ratio $[B]/[C]$ can be evaluated [10] from $K_6/(K_4[H^+])$ to be 0.0015 at pH=3, 15 at pH=7, and 1 500 at pH=9, showing that due to equilibrium the almost colorless carbinol is predominant in alkaline solutions, all these numerical values referring to HO (MG) and MG^+ . The ratio $[B]/[S']$ is already 80 at pH=1 and 8000 at pH=3.

Excited-State Relaxation and Photochemical Bleaching

That aq. green MG^+ solutions slowly fade at pH above 6 (as mentioned above) may be due to the simple addition of H_2O to give HO(MG). However, the polarographic results [10] leave the possibility of forming reduced semiquinone products (conceivably colored, but much less intensely than CR_3^+ species). Thus, 26 micromolar $MG^+ HO_2CCO_2^-$ in EtOH is almost colorless after 3–60 d in daylight, with a very weak band remaining at 580 nm (Fig. 3). Then, addition of HNO_3 to make pH=1 recovers the spectrum of the green MG^+ .

The Brønsted acidity of $H(MG)^{2+}$ etc. and the Lewis anti-bases CR_3^+ reacting with terminal oxide groups of gel glasses are likely to render the chemistry of triphenylmethane (and related intense) colorants quite unexpected. In particular, the sol-gel method [2][3] is likely to permit observations on immobilized cations and molecules.

Experimental results on the excited state sol-gel glasses prepared from $(MeO)_4Si$ and containing blue-green MG^+ show [2] three absorption bands, typically

at 605–616 nm due to the first excited singlet S_1 , a weaker maximum at 411–421 nm due to a second S_2 (in aq. solutions [7][11][12] at 618 nm and 424 nm), and a third band at 312 nm ascribed to S_3 . Not only the MG^+ cation emits a broad band at 650 nm (representing a Stokes shift of S_1), but light absorption in S_2 provides an additional emission band at 470 nm, and in S_3 still a third band at 360 nm [2]. Hence, a cascade transition allows emission of Stokes-shifted S_2 and S_1 from S_2 excitation, and from all three S_n when illuminated at 300–320 nm, the highest energy centered around 26315 cm^{-1} .

Conclusions

Malachite Green exists in glasses as well as in other viscous materials as a strongly colored monocation or as a weaker colored dication with the central C-atom having three carbon neighbors. Upon illumination or with addition of a base, the cations are changed reversibly to the almost colorless carbinol form in which the central atom acquires fourfold coordination. The dark green monocation in glasses exhibits fluorescence from S_3 , S_2 , and S_1 excited states. The quantum efficiency of the S_1 luminescence is about 20% at room temperature indicating relatively low nonradiative losses in this medium.

Under special experimental conditions, mainly using strong acids as catalysts for the formation of gel glasses, a purple form (possibly a complexed monocation) is formed which may also produce a shoulder close to 560 nm in the absorption spectrum of the green form (unless this is a vibronic excitation of S_1 , or an excited singlet with a molar extinction coefficient of $e \approx 10^4$ situated between S_1 and S_2). In the ethanolic solution (Fig. 3) MG^+ may be bound to oxalate anions.

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- [1] M. Canva, G. LeSaux, P. Georges, A. Brun, F. Chaput, J.P. Boilot, *Chem. Phys. Lett.* **1991**, 176, 495.
- [2] V. Chernyak, R. Reisfeld, *Chem. Phys. Lett.* **1991**, 181, 39.
- [3] R. Reisfeld, C.K. Jørgensen, *Struct. Bonding* **1991**, 77, 207.
- [4] W.R. Orndorff, R.C. Gibbs, S.A. McNulty, C.V. Shapiro, *J. Am. Chem. Soc.* **1927**, 49, 1541, 1545.
- [5] H.J. Dauben, L.R. Honnen, K.M. Harmon, *J. Org. Chem.* **1960**, 25, 1442.
- [6] M.P. Doyle, D.J. DeBruyn, D.J. Scholten, *J. Org. Chem.* **1973**, 38, 625.
- [7] R. Cigén, *Acta Chem. Scand.* **1958**, 12, 1456; *ibid.* **1960**, 14, 973; *ibid.* **1961**, 15, 1905.
- [8] R. Cigén, C.G. Ekström, *Acta Chem. Scand.* **1963**, 17, 2083; *ibid.* **1964**, 18, 157.
- [9] C.G. Ekström, *Acta Chem. Scand.* **1965**, 19, 1381; *ibid.* **1966**, 20, 444.
- [10] G. Bengtsson, *Acta Chem. Scand.* **1967**, 21, 1138, 2544.
- [11] C.D. Ritchie, W.F. Sager, E.S. Lewis, *J. Am. Chem. Soc.* **1962**, 84, 2349.
- [12] A. Granzow, A. Wilson, F. Ramirez, *J. Am. Chem. Soc.* **1974**, 96, 2454.
- [13] Th. Förster, G. Hoffmann, *Z. Phys. Chem. N.F.* **1971**, 75, 63.
- [14] M.D. Hirsh, H. Mahr, *Chem. Phys. Lett.* **1979**, 60, 299.
- [15] T. Robl, A. Seilmeier, *Chem. Phys. Lett.* **1988**, 147, 544.
- [16] M.M. Martin, E. Breheret, F. Nesa, Y.H. Meyer, *Chem. Phys.* **1989**, 130, 279.
- [17] E.P. Ippen, C.V. Shank, A. Bergman, *Chem. Phys. Lett.* **1976**, 38, 611.
- [18] R. Gvishi, R. Reisfeld, M. Eisen, *Chem. Phys. Lett.* **1989**, 161, 455.
- [19] R. Gvishi, R. Reisfeld, *J. Non-Cryst. Solids* **1991**, 128, 69.
- [20] M. Eyal, R. Reisfeld, V. Chernyak, L. Kaczmarek, A. Grabowska, *Chem. Phys. Lett.* **1991**, 176, 531.
- [21] G.N. Lewis, D. Lipkin, T.T. Magel, *J. Am. Chem. Soc.* **1941**, 63, 3005.
- [22] J. Bjerrum, *Naturwissenschaften* **1951**, 38, 461.
- [23] C.K. Jørgensen, *Chimia* **1974**, 28, 605.
- [24] C.K. Jørgensen, *Topics Curr. Chem.* **1984**, 124, 1; *ibid.* **1989**, 150, 1.
- [25] N. Ingri, G. Lagerström, M. Frydman, L.G. Sillen, *Acta Chem. Scand.* **1957**, 11, 1034.
- [26] M.M. Martin, *Chem. Phys. Lett.* **1975**, 35, 105; *ibid.* **1976**, 43, 332.
- [27] R. Reisfeld, M. Eyal, R. Gvishi, *Chem. Phys. Lett.* **1987**, 138, 377.
- [28] R. Cigén, *Acta Chem. Scand.* **1962**, 16, 1271.