of a histidine molecule and to the carboxylic group of the other histidine molecule. Simultaneously Cu^{II} would be bound glycine-like to a ligand molecule and histamine-like to the other. This not only because the thermodynamic parameter values obtained (Table VII) are, on the whole, the most close to the experimental ones (Table V) but also because the hypothesis accounts for the enthalpic and entropic trend of the heteronuclear complexes $[CuNi(his)_2]^{2+}$, $[CuZn(his)_2]^{2+}$, and $[CuCd(his)_2]^{2+}$. In fact, with examination the other two possible hypotheses (Zn^{II} coordinates to two carboxylic oxygens or to two imidazole nitrogens of two different L-histidine molecules) the difference between the formation $\Delta H°$ of the two species $[CuZn(his)_2]^{2+}$ and $[CuCd(his)_2]^{2+}$ should clearly be higher than that found, owing to the more "soft" character of Cd^{II} compared with Zn^{II}.

The positive and fairly large entropic contribution, consequent to the formation of these binuclear complexes, in spite of the "stiffening" of the ligand coordinated to two different metal ions, can be accounted for by hypothesizing a "secondary" interaction between Ni^{II}, Zn^{II}, or Cd^{II} with the neighboring donor atoms "primarily" bound to Cu^{II}. This interaction would encourage Cd^{II} and Zn^{II} more than Ni^{II} desolvation, following a trend that can be related to the different tendency to six-coordination of the above metal ions (Ni > Cd > Zn and $\Delta S° = 25$, 29, and 32 eu).

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Registry No. L-Histidine, 71-00-1; histamine, 51-45-6; Cu, 7440-50-8; Ni, 7440-02-0; Zn, 7440-66-6; Cd, 7440-43-9.

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Copper Halide Containing Photochromic Glasses

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The melting and characterization of photochromic alkali aluminoborosilicate glasses containing copper halide are reported. The glasses have high initial transmittance (72–86%) and can darken to 14% under simulated solar irradiation. The darkened glass absorption spectrum is broad, maximizing at 580 nm. A process for darkening is proposed in which copper colloids are formed. Photochromism is demonstrated in glasses of 44–51 cation % silica. At any given silica and alumina level, a certain alkali to boric acid ratio is necessary to achieve photochromism. This ratio decreases as silica and alumina increase.

Photochromic glasses containing a number of different crystallites in suspension have been reported.[1] Metal halides[2] and silver halides[3] in particular have received considerable attention. Silver halide containing glasses have found application in ophthalmic ware and have been proposed for use in automotive and architectural glazing.

The photochromic characteristics of silver halide containing glasses vary considerably with glass composition, but certain properties are common to all the glasses. Glasses containing silver halide darken in response to UV or longer wavelength visible light. Thermal and optical fading rates are sensitive to both base glass composition and "photochromic element" addition (silver, halogen, and copper). Silver halide containing glasses show varying degrees of temperature dependence of the steady-state darkening level and are subject to a maximum temperature limit above which no darkening will be observed.

Several photosensitive copper compounds have been reported. Darkening upon irradiation has been observed for CuCl(s) and CuBr(s) in suspension in aqueous solution and in gelatine.[4] $CuC_2O_4{\cdot}{}^1/_2H_2O$ has been examined[5] as a potential high-speed photographic material. In these cited studies and in the work of Roginskii et al.[6] on the same compounds, the principle products of photolysis are Cu and Cu_2O. A photochromic reverse reaction is not noted in any of these studies. Tsekhomskii[7] has reported a CuCl-containing glass which shows photochromic darkening and fading, although crystallite size is estimated at considerably greater than 100 Å causing reduced transmittance due to scattering before photochromic darkening.

The characterization of a range of copper halide containing photochromic glasses which show high initial transmittance and photochromic response similar to silver halide containing glasses is now communicated. Base glasses have been examined in a mixed-alkali aluminoborosilicate system, with variation in the photochromic elements Cu, Cl, Br, and F. Photochromic properties of the glasses have been examined from the standpoint of pertinent parameters such as darkening level, spectral response, thermal bleaching rate, temperature dependence of darkening, and induced absorption spectrum. The examination of these data allows speculation on the photochromic mechanism in copper halide photochromic glasses.

Experimental Section

All glasses were batched with use of reagent grade batch materials and melted in covered 500-cm³ platinum crucibles. Glass was melted in Glo-bar furnaces at 1400 °C and stirred before being poured into slabs and annealed at 375–450 °C overnight. After annealing, samples of the glasses were subjected to heat treatment to develop photochromism, typically at a temperature between 580 and 680 °C for 10–60 min. All operations were performed in air. Some atmospheric control of redox conditions is possible, but compositional control is

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Table I

A. Alkali:B_2O_3 Ratio Effect on Copper Halide Photochromism

	A	B	C	D	E
			Composition		
SiO_2	44.36	44.36	44.36	44.36	44.36
B_2O_3	21.5	22	22.5	23	23.5
Al_2O_3	10.8	10.8	10.8	10.8	10.8
Na_2O	13.2	12.7	12.2	11.7	11.2
Li_2O	6.4	6.4	6.4	6.4	6.4
K_2O	1.5	1.5	1.5	1.5	1.5
alkali:B_2O_3	0.98	0.94	0.89	0.85	0.81
			Color		
as melted	blue-green	green	green	green	yellow-green
heat treated (600 °C, 45 min)	light green	green	brownish green	red-brown	deep red-brown
			Transmittance		
T_i[a]	d	80	80	77	d
$T_{D_{10}}$[b] (27 °C)	d	65	34	35	d
F_5[c] (27 °C)	d	9	19	16	d

B. Batched Photochromic Element Levels, Glasses A–E (Weight Percent Over 100% Base Glass)

CuO	0.58	WO_3	0.30
Cl	0.405	As_2O_3	0.40
Br	0.45		

[a] Transmittance before darkening (human eye response filter). [b] Transmittance after 10-min darkening. [c] Transmittance points of fade in 5 min. [d] Not photochromic.

more exact. The samples were then ground and polished to 2 mm thickness for measurement of photochromic properties. Photochromic properties were measured in a temperature-regulated cell capable of maintaining a constant temperature between −30 and +60 °C. The source of illumination was a xenon arc lamp filtered to closely approximate solar irradiation. Spectral response of darkening was examined by filtering the simulated solar spectrum or by using an Hg lamp filtered to give light primarily from 300–400 nm in conjunction with a Spectra-Physics Model 165 Kr–Ar ion laser. The induced absorption spectrum was analyzed with use of the same type of darkening source in conjunction with a rapid scan spectrophotometer capable of measuring induced absorption between 400 and 750 nm. The spectrum is measured at 10 separate wavelengths simultaneously in 10–100 ms, with data collected and displayed by a CRT equipped PDP 11/04 minicomputer.

Results

A. Composition. All the compositions can be viewed as an alkali aluminoborosilicate base glass to which has been added a number of photochromic species, e.g., copper, chloride, bromide, fluoride, iodide, molybdenum, and tungsten. Both base glass and photochromic elements will affect photochromism. At an established SiO_2 and Al_2O_3 level, photochromism will be observed only within a narrow alkali:B_2O_3 ratio range as shown in Table IA.

From the color of the glasses in Table IA it is seen that, as the alkali:B_2O_3 ratio is lowered, the color is changed from blue (oxidized, Cu^{II} containing) to yellow (reduced, Cu^{I} containing) and that a necessary condition of photochromism is that significant amounts of both Cu^{I} and Cu^{II} must be present in the glass prior to heat treatment. Cu^{II} does not participate in the proposed darkening mechanism; its presence seems necessary only in indicating that the glass is not too reduced to be photochromic after heat treatment. Glass C demonstrates this optimum condition. Table IB lists the photochromic elements present in glasses A–E. As_2O_3 is listed in Table IB not strictly as an element which participates in the photochromic darkening but as necessary addition for the observation of copper halide photochromism. At the correct alkali:B_2O_3 ratio, then, the redox action of As_2O_3 during the glass-melting process helps to allow the copper to achieve the necessary oxidation state. Due to volatilization during melting, only 0.1 wt % As_2O_3 remains in the glass after melting, limiting variation in the As_2O_3 level to effect the redox state. The appearance of the red-brown color at lower alkali:B_2O_3 ratios after heat treatment also is indicative of the instability of the copper oxidation state and may be due to some deposited copper colloids and/or copper ruby formation. Copper ruby is strongly colored red glass in which copper colloids near 1000 Å in size are precipitated with the glass network.[8] The deposited copper may be located on the surface of copper halide photochromic particles, a supposition supported by the absence of any red color after heat treatment in halide-free glasses. Alternatively the halide may be active in nucleating copper colloids.

Table II. Silica Effect on Copper Halide Photochromism[a]

	F	G	H	I	J	K	L	M	N
					Composition				
SiO_2	45	45	45	49	49	49	51	51	51
B_2O_3	23.3	23.3	23.3	24.3	23.8	22.8	23.3	23.3	23.3
Al_2O_3	11	11	11	9	9	9	9	9	9
Na_2O	11.9	10.9	9.9	8.9	9.4	10.4	9.4	8.9	9.9
Li_2O	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
K_2O	1.6	2.6	3.6	1.6	1.6	1.6	1.1	1.6	1.1
					Transmittance				
T_i	85	85	86	78	72	79	79	79	77
$T_{D_{10}}$	43	41	61	29	14	22	14	16	14
F_5	16	15	10	12	13	17	14	16	14

[a] Photochromic element batched levels listed in Table IB.

It has been demonstrated[9] in studies on silver halide containing photochromic glasses that precipitation of silver halide is responsive to changes in the host glass composition. The amount of silver halide which can be precipitated is proportional to the difference in halogen solubility at the melting temperature of the glass and the heat treatment temperature. Halogen solubility in turn relates to the number of nonbridging oxygens present in the host glass. The number of nonbridging oxygens is dependent on boron coordination, which is temperature sensitive. At the heat treatment temperature, then, precipitation of silver halide depends upon achieving a change in the number of nonbridging oxygens. The amount of alkali present which can form alkali–oxygen–boron bonds will, therefore, control the precipitation process. The same type of process is postulated in copper halide photochromism.

The silica level in the base glass has been varied over a small range, from 45 to 51 cation %. At each silica level there is an optimum alkali:B_2O_3 ratio; maximum photochromic response is observed at lower total alkali or lower alkali:B_2O_3 ratios as the silica level is raised. The alkali balance, Na_2O:Li_2O:K_2O, can also affect the photochromism; as can be seen in Table II, the 2% K_2O/Na_2O exchange between glass F and glass H weakens the photochromic response considerably.

B. Photochromic Elements. Copper oxide and ionic chloride and bromide are necessary to achieve any photochromism. Fluoride, tungstate, and molybdate can each strongly affect photochromic response but are not sufficient to provide photochromism without the primary three photochromic elements.

The level of copper oxide which can be used is critical; photochromism ceases outside the range 0.6–1.2 wt %. Both bromide and chloride together seem to be necessary to achieve good darkening within the composition ranges examined, although the glasses are less sensitive to halide variations than most silver halide containing glasses. A change from 0.4 to 0.3 wt % batched does not have a noticeable effect on photochromic properties.

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Table III

T, °C	T_i	$T_{D_{60}}$	F_5
60	87	48	24
40	87	38.5	20.5
20	87	28	13
0	87	27	8
−18	87	25	5.5

Tungstate is instrumental in achieving high darkening levels in these glasses. Its most important role may be its effect on the precipitation of the photochromic phase from the glass upon heat treatment. Alternatively, it could be active as a dopant in the copper halide rich photochromic particles, although this possibility seems unlikely due to the high levels ($\sim$1.0 wt %) necessary to achieve its action.

Fluoride can affect a balance between the best darkening levels and the haze observed in the glass, but it is not critical to photochromism. This indicates that fluoride is probably participating as a nucleating agent only.

C. Photochromic Properties. Copper halide photochromic glasses darken from an initial green color which transmits 75–88% of the incident visible light to a gray or gray-brown darkened color. The compositions which show the greatest dynamic range darken to about 15% transmittance at 27 °C in 2.0 mm thickness under simulated solar radiation (see Table II) and fade 15–25 transmittance points in 5 min.

Some temperature dependence of darkening is observed, as shown in Table III. This temperature dependence is at least as low as that observed for the least temperature dependent silver halide containing photochromic glasses. The considerable darkening at 60 °C is particulary notable. While initial fade may be rapid, all the glasses melted exhibit at least some residual color for long times (2–10 h) after darkening, and complete fading may take several days.

Copper halide photochromic glasses will darken under irradiation wavelengths from 350 nm to at least 650 nm. Experimental work on initial darkening rates has shown a finite incubation period for colloid growth in silver halide photochromics. Such a time lag is not observed in copper–cadmium-containing photochromics.[10] In the latter glasses it is felt that a color center trapping mechanism rather than colloid growth gives rise to the observed absorption. Under UV light, copper halide glasses show a finite initial darkening rate, while under visible irradiation there is a time lag after the start of irradiation before darkening begins. The fading behavior is also a function of the wavelength of the light used to darken the glass in Figure 1. The glass as depicted in Figure 1 shows that, after UV darkening, the fade of the copper halide glasses is almost linear. Under visible radiation, though, fading is exponential, with a fast initial fade which rapidly decreases. These data can be explained by a process in which the initial step, which occurs under UV light and is a relatively high-energy process, produces intermediate trapped electrons and holes which, in general, behave similarly to those produced in copper–cadmium photochromic glasses. The exception to copper–cadmium-type photochromic behavior is that the glass without cadmium is then susceptible to further darkening upon irradiation possibly with the formation of copper colloids, as in eq 1. It is curious that process 1 would occur with low-

$$\mathrm{Cu}^+ \xrightarrow{h\nu} \mathrm{Cu}^{2+} + \mathrm{Cu}^0\ \text{(colloid)} \qquad (1)$$

energy visible light and not with higher energy light, and in fact process 1 may ocurr with UV as well as with visible light after the initial high-energy process. The postulated mechanism is supported by the observation that darkening with visible light is very slight until after sensitization with UV light. Less than half the maximum achievable darkening occurs with only visible light. The UV produced species does not persist after thermal bleaching at 100 °C for several hours. Not only does UV light give some darkening then, it also produces states prone to darkening under visible irradiation.

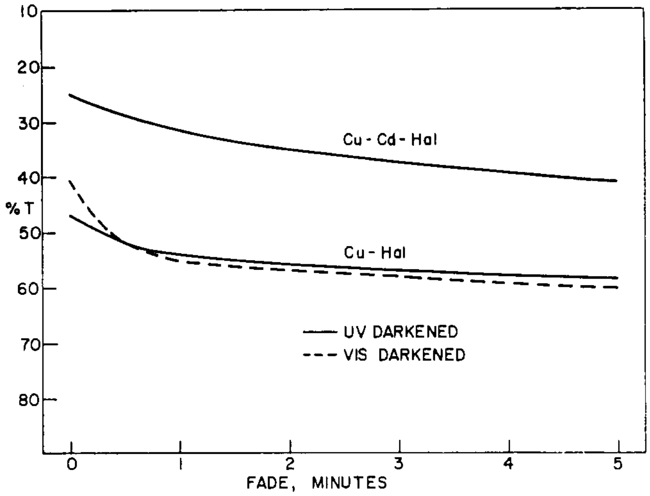

Figure 1. Fade of copper halide containing photochromic glass after visible and UV light darkening, as compared to copper–cadmium halide.

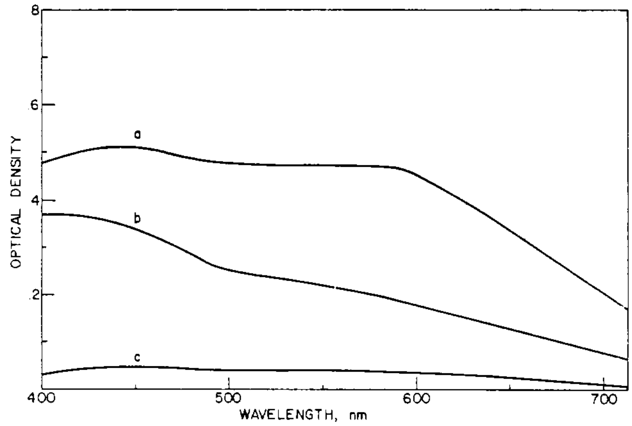

Figure 2. Spectra of absorbing species in darkened copper halide photochromic glass; corrected for contribution of bulk glass and for reflection. In (a) the glass has been sensitized with UV (Corning Glass Works 7-54 filter) and then darkened with visible (3-68). In (b) just visible darkening is shown, and in (c) just UV darkening is shown. Note the lower absorption in (b) and (c).

Further evidence for two separate processes is provided through examination of darkened absorptions measured with use of a rapid scan spectrophotometer equipped with a darkening source. Using this apparatus, it is possible to darken the sample glass with just visible or just UV light. Figure 2 shows three spectra of glass K after UV, visible, and UV-sensitized visible darkening, respectively. Under sensitized and unsensitized visible darkening, spectral maxima are present at 450 and 580 nm, in constrast to the UV darkened glas spectrum. The UV-sensitized, visible light darkened spectrum is similar but darker. Calculations [with use of the literature values of optical constants[11] of metallic copper the wavelength corresponding to the peak can be determined from the formula $C_{\mathrm{abs}} = \pi a^3(-8\pi/\lambda)I_{\mathrm{m}}(\epsilon - n_0^2)/(\epsilon - 2n_0^2)$, where $\epsilon_{\mathrm{Cu}} = \epsilon + i\epsilon_2$, a = particle size] on the expected absorption of copper colloids

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in copper chloride predict an absorption maximum at 575 nm, which is, in fact, very close to the observed maximum under visible irradiation. The formation of copper colloids is thus proposed. The possibility of copper colloid formation is supported by work on photochemical disproportionation in the CuCl(s)–H_2O(l) system in which the induced spectrum has been identified as copper colloids (18–30 Å, oblate).[12] It is important to note that copper colloids formed within a copper halide crystallite will be gray-brown in color as opposed to the red color shown by copper colloids in a glassy matrix due to the higher refractive index of the copper halide crystallite. In the glasses, however, the presence of colloids has been difficult to establish. No optical bleaching of the darkened glass is observed at accessible wavelengths into the near infrared nor does darkening with a polarized source produce any observable dichroism. The phenomenon of polarizability helps to establish the colloidal nature of the absorbing species in darkened silver halides.[13] The colloidal nature of the darkened copper halide photochromics is nonetheless supported by the spectral data and fade characteristics.

Conclusions

All present evidence indicates that the copper halide containing glasses give rise to a unique photochromic glass system. The photochromic behavior is particularly notable from the standpoint of the low-temperature dependence of darkening, including the darkening observed at temperatures near 60 °C.

These glasses as described do not equal the performance of silver halide containing photochromic glasses with respect to speed of darkening and fading; however, applications may exist where the cost and/or availability of silver would restrict the use of silver halide photochromism.

Registry No. SiO_2, 7631-86-9; B_2O_3, 1303-86-2; Na_2O, 1313-59-3; Li_2O, 12057-24-8; K_2O, 12136-45-7; CuO, 1317-38-0; Cl, 7782-50-5; Br, 7726-95-6; WO_3, 1314-35-9; As_2O_3, 1327-53-3.

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Laser-Excited Luminescence Study of the Chain Compound $BaPd(CN)_4{\cdot}4H_2O$

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Luminescence studies from 5 to 290 K on single crystals of the chain compound $BaPd(CN)_4{\cdot}4H_2O$ show the presence of a short-lived component (<10 ns) centered at about 26 × 10^3 cm^{-1} and a long-lived (2 ms at 5 K) component at about 19 × 10^3 cm^{-1}. The 26 × 10^3 cm^{-1} transition shows a strong temperature dependence which is shown to result from the changing metal–metal separation. Differences of lifetimes and emission energies between palladium and platinum chain compounds are explained as a result of the smaller spin–orbit coupling for palladium. Comparison to $BaPt(CN)_4{\cdot}4H_2O$ suggests that the palladium salts will not be good candidates for one-dimensional-like conductors.

Introduction

Recent years have seen much interest in the square-planar platinum tetracyanide compounds. The best known example of these is KCP ($K_2Pt(CN)_4Br_{0.3}{\cdot}3H_2O$), which exhibits extremely anisotropic electrical conductivity and also displays a prototypical Peierls distortion-like phase transition at low temperatures.[1] In an effort to better understand the role of bonding in KCP, a number of studies, particularly by Yersin and co-workers,[2-5] have been carried out on a series of nonconducting platinum chain compounds which can serve as prototypes to KCP. The effect of metal–metal interactions on the spectroscopic properties have been quantified, and the role of the structure on the conductivity properties has become better understood.

Palladium tetracyanides are also known to form chain compounds,[6] and it becomes interesting to ascertain whether the observations and concepts for the $5d^8$ platinum compounds carry over to the $4d^8$ palladium compounds. In this work we have studied $BaPd(CN)_4{\cdot}4H_2O$ which is one of these linear chain compounds. According to early X-ray studies[7] it crystallizes in a monoclinic space group C_{2h}^6 and has chains of $Pd(CN)_4{}^{2-}$ anions separated by 3.37 Å at room temperature. This is an intermediate distance with respect to platinum compounds where the distances have ranged approximately from 2.87 to 3.67 Å.

Experimental Section

Single crystals of $BaPd(CN)_4{\cdot}4H_2O$ were grown by slow evaporation of aqueous solutions. These crystals were either mounted in an Air Products Helitran for variable-temperature measurements down to 5 K or immersed in small quartz liquid-nitrogen Dewars for 77 K. Care was taken to avoid dehydration which can occur easily for these crystals. Luminescence excitation was generally at 337.1 nm by a Molectron Model UV14 nitrogen laser. Emission was detected by an RCA 31034 A-20 response phototube mounted on a McPherson scanning monochromator.

Lifetime measurements were made with a Princeton Applied Research Model 162 boxcar integrator. Excitation was provided by the pulsed nitrogen laser with pulses approximately 5 ns in length. Shorter lifetimes than this could normally be expected to be deconvoluted, but electronic drift precluded accurate lifetime measurements less than 10 ns.

Observations

No emission from $BaPd(CN)_4{\cdot}4H_2O$ was apparent at room temperature but cooling to 77 K yielded visually intense luminescence. A typical spectrum obtained at 7 K is shown in

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