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Hexamethylenetetramino Copper Iodide Complexes and Their Luminescence Properties

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Copper(I) iodide reacts with hexamethylenetetramine to form different strongly fluorescent complexes, depending on preparation methods and solvents used.

If methanol or ethanol is used as solvent, the products alter their yellow room temperature fluorescence colour in red or violet respectively at 77 K, i.e. show the very interesting phenomenon of fluorescence thermochromism.

But if the structure is tightened by a better supply of hexamethylenetetramine or a second nitrogen base is involved thermochromism ceases. Foreign nitrogen bases which are coordinated to the copper iodide complexes can be evaporated or re-adsorbed with characteristic variation of luminescence properties; and the compound $3CuI \cdot (CH_2)_6N_4 \cdot 2C_5H_5N$ *phosphoresces after being excited by the 254 nm radiation at 77 K, a weaker ultra violet light being uneffective.*

Introduction

Since R. T. Randall[1] mentioned two different fluorescence colours of copper(I) chloride at low temperatures in 1938, no more investigations about this interesting phenomenon seem to have followed until H. D. Hardt and H. D. De Ahna[2]. H. D. Hardt and H. Gechnizdjani[3,4] reported that complexes of copper(I) halides and several pyridine derivatives not only fluoresce in ultra violet light, but often are able to change their fluorescence colour in a reversible manner on cooling the sample in liquid nitrogen.

The term *Fluorescence Thermochromism* had been proposed for this effect.

As chloroplumbates(II) do only fluoresce at low temperature but also change their fluorescence colour to a certain extent, E. A. Bozhevolnov, E. A. Soloviev and N. A. Lebedeva[5] used the shift of fluorescence emission from 385 nm at 77 K to 490 nm at 203 K to determine traces of lead, simply by registration of the green 490 nm emission during unfreezing of the intensely cooled hydrochloric solutions.

Copper(I) complexes with nitrogen bases were, however, never observed to fluoresce in solution, and thermochromism seems only to occur with monosolvates of the type $CuX \cdot L$ ($X = Cl^-, Br^-, I^-, CN^-, SCN^-$; L = pyridine derivatives, other aromatic nitrogen bases, and some aliphatic amines). Thus for instance, $CuI \cdot (C_5H_5N)_3$ is not fluorescent at room temperature, $CuI \cdot (C_5H_5N)_2$ fluoresces green but is not thermochromic, and $CuI \cdot (C_5H_5N)$ fluoresces yellow at 300 K but violet at 77 K.

Because cuprous iodide reacts with hexamethylenetetramine apparently to form different complexes with different luminescence properties depending on the solvents and methods used, a more detailed investigation of this subject became desirable.

Experimental

Hexamethylenetetramine, $(CH_2)_6N_4$, in spite of its multidentate character, reacts with aqueous solutions of $K(CuI_2)$ to form a dark yellow fluorescent complex which analyses as $CuI \cdot (CH_2)_6N_4$; there is no change in fluorescence emission while cooling it from 300 to 77 K.

$CuI \cdot (CH_2)_6N_4$ *from Aqueous Solution*

A solution of 2.8 g (0.02 mol) of hexamethylenetetramine in 10 ml water is added to an aqueous solution of 1.9 g (0.01 mol) of copper(I) iodide and 20 g (0.12 mol) of potassium iodide in 10 ml water. The precipitate should be washed at least five times with 25 ml water, filtered and dried at room temperature. However when cuprous iodide suspensions in methanol or ethanol react with hexamethylenetetramine, the products fluoresce yellow and prove to be thermochromic on cooling in liquid nitrogen (Table I).

$8CuI \cdot (CH_2)_6N_4 \cdot 2CH_3OH$

A suspension of 0.95 g (0.005 mol) of copper(I) iodide in 100 ml methanol is added to 0.7 g (0.005 mol) of powdered hexamethylenetetramine and stirred for about 50 hr at room temperature. The product can be dried at 300 K after filtering without previous washing.

TABLE I. Fluorescence properties and analytical data of copper(I) iodide complexes.[a]

No	Formula of Complex	Fluorescence 300 K	Colour 77 K	% Cu calc.	% Cu found.	% Hexameth. calc.	% Hexameth. found	% Other Ligands	Remarks
1	$CuI \cdot (CH_2)_6N_4$	yellow	yellow	19.39	18.34	42.72	42.8		
2	$8\ CuI \cdot (CH_2)_6N_4 \cdot 2\ CH_3OH$	yellow	red	29.7	29.22	8	7.99	3.71 CH_3OH	calc.
								3.53 CH_3OH	fd.
3	$8\ CuI \cdot (CH_2)_6N_4 \cdot 2\ C_2H_5OH$	yellow	violet	29.79	28.3	7.99	8.2	5.25 C_2H_5OH	calc.
								5.10 C_2H_5OH	fd.
4	$2\ CuI \cdot (CH_2)_6N_4 \cdot 4\ CH_3CN$	yellow	yellow	18.71	17.6	20.47	19.0	24.4 CH_3CN	calc.
								25.6 CH_3CN	fd.
5	$3\ CuI \cdot (CH_2)_6N_4 \cdot 2\ C_5H_5N$	blue	blue	21.9	21.6	16.13	17.5	18.22 C_5H_5N	calc.
								18.5 C_5H_5N	fd.
6	$3\ CuI \cdot (CH_2)_6N_4 \cdot (2+x)C_5H_5N$	green	green						
7	$2\ CuI \cdot (CH_2)_6N_4$	yellow	yellow	24.62	25.0	26.92	26.8		from thermal decomp. of (4)
8	$3\ CuI \cdot (CH_2)_6N_4$	yellow	yellow	27.04	27.0	19.72	20.0		from thermal decomp. of (5)

[a] Copper analyses was carried out by titration with E.D.T.A.; other analyses were performed by usual microanalytical methods and thermo balance measurements.

$8CuI \cdot (CH_2)_6N_4 \cdot 2CH_3CH_2OH$

Same procedure, however with 100 ml ethanol as solvent.

If two different nitrogen bases react simultaneously with copper(I) iodide, the resulting products are non-thermochromic but eventually strongly blue fluorescent.

$2CuI \cdot (CH_2)_6N_4 \cdot 4CH_3CN$

1.9 g (0.01 mol) of copper(I) iodide and 1.4 g (0.01 mol) of hexamethylenetetramine in 100 ml acetonitrile are stirred for about 12 hr to form a colourless but *yellow* fluorescent and non-thermochromic product. After additional 30 hr of stirring the mixture, the sample can have adsorbed a certain surplus of acetonitrile to form a very unstable solvate which is distinguished from the original tetrasolvate by its *blue* fluorescence.

$3CuI \cdot (CH_2)_6N_4 \cdot 2C_5H_5N$

A saturated solution of hexamethylenetetramine in methanol (at 300 K approx. 74 g per liter) is added to a solution of 0.95 g (0.005 mol) copper(I) iodide in 10 ml pyridine.

The precipitate is dried at room temperature without washing.

Results

Properties

The solvates with alcohols, pyridine and acetonitrile (Table I) are stable at room temperature for at least several weeks, in contrast to products which may be obtained by adsorption of further pyridine or acetonitrile molecules. All products are obtained as finely divided powders and there is no possibility of recrystallizing them from organic solvents without decomposition. Nevertheless the precipitates are homogeneous and do not contain any residual particles of cuprous iodide.

X-ray data are given in Table II, where the values for the three first and most intense interferences are underlined.

The solvates which contain other ligands besides hexamethylenetetramine decompose and desorb their solvate molecules above 380 K to form residues which contain merely cuprous iodide and hexamethylenetetramine in given ratios. Thus, $3CuI \cdot (CH_2)_6N_4 \cdot 2C_5H_5N$ yields $3CuI \cdot (CH_2)_6N_4$, and $2CuI(CH_2)_6N_4 \cdot 4CH_3CN$ yields $2\ CuI \cdot (CH_2)_6N_4$. These residues fluoresce yellow with nearly the same spectra as is observed with $CuI \cdot (CH_2)_6N_4$ itself (Figure 1).

The hexamethylenetetramine component is destroyed only above 550 K to form pure cuprous iodide as a residue. The residues which contain merely a complex of cuprous iodide and hexamethylenetetramine are finely divided by evaporation of their former sol-

TABLE II. X-ray Data of Some Hexamethylenetetramino Copper(I) Iodide Complexes Obtained by Powder Photographs with Copper K_a Radiation (the three first strong or very strong interferences are underlined. vst = very strong, st = strong, m = medium, w = weak).

$CuI\cdot(CH_2)_6N_4$

d	I
4.008	st
3.488	m
2.892	m
2.830	w
2.473	vst
2.113	m
2.020	w
1.962	st
1.877	w
1.757	w
1.727	w
1.683	w
1.615	w
1.563	w
1.542	w
1.476	w
1.404	w

$3CuI\cdot(CH_2)_6N_4$

d	I
8.029	m
3.863	st
2.851	w
2.534	m
2.117	w
1.958	m

$2CuI\cdot(CH_2)_6N_4$

d	I
8.161	vst
7.070	w
4.058	vst
3.531	m
3.207	w
2.870	st
2.702	m
2.483	st
2.361	w
2.117	st
1.967	st
1.834	w
1.756	w
1.715	w
1.663	w
1.615	w
1.549	w

$2CuI\cdot(CH_2)_6N_4\cdot(2+x)C_5H_5N$

d	I
8.253	st
5.240	w
4.457	w
4.270	st
4.047	st
3.792	w
3.678	w
3.496	w
3.292	w
2.986	w
2.840	w
2.735	w
2.681	w
2.610	w
2.424	w

$8CuI\cdot(CH_2)_6N_4\cdot 2\ C_2H_5OH$

d	I
7.942	m
4.044	st
3.469	m
2.854	m
2.499	st
2.397	w
2.121	st
1.967	m
1.754	m

$8CuI\cdot(CH_2)_6N_4\cdot 2CH_3OH$

d	I
3.599	st
3.440	st
3.006	w
2.557	m
2.497	m
2.180	w
2.127	m
2.086	st
1.964	w
1.934	w
1.815	st
1.626	w

$3CuI\cdot(CH_2)_6N_4\cdot 2C_5H_5N$

d	I
10.048	st
9.025	m
4.270	m
4.095	m
2.755	m
2.585	m
2.462	w
2.161	w
2.143	w
1.988	w

$3CuI\cdot(CH_2)_6N_4\cdot(2+x)\ C_5H_5N$

d	I
11.481	m
8.638	m
7.255	m
4.497	w
4.336	st
4.118	w
2.925	w
2.745	w
2.640	w
2.525	w

$8CuI\cdot(CH_2)_6N_4$

d	I
4.026	m
3.477	st
2.483	m
2.129	w
2.031	m
1.764	w
1.583	w
1.449	w

$2CuI\cdot(CH_2)_6N_4\cdot 4CH_3CN$

d	I
9.044	vst
6.100	st
5.079	vst
4.493	st
3.058	m
2.876	w
2.765	w
2.381	w
2.219	w
2.129	w

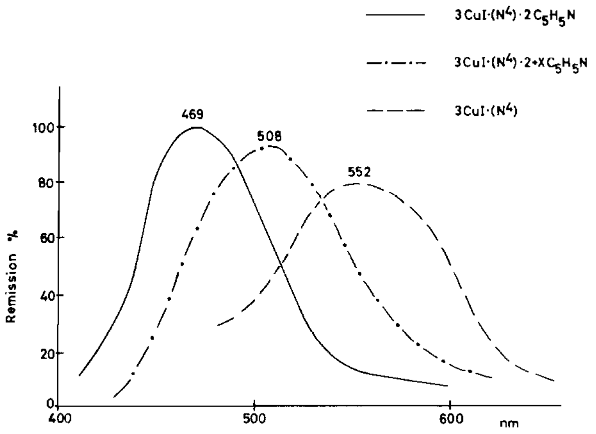

Figure 1. Fluorescence spectra of different complexes, based on $3CuI\cdot(CH_2)_6N_4$. (N^4) symbolizes hexamethylenetetramine, $(CH_2)_6N_4$, x≈2.

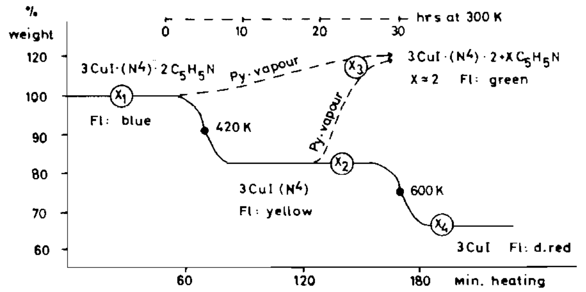

Figure 2. Thermal decomposition and re-absorption of $3CuI\cdot(CH_2)_6N_4\cdot 2C_5H_5N$ with respective fluorescence colours (Fl). Py = pyridine, (N^4) = Hexamethylenetetramine; X_1–X_4: samples taken for X-ray diffraction, $X_1 \neq X_2 \neq X_4$; $X_1 = X_3$, X_4 = copper(I) iodide.

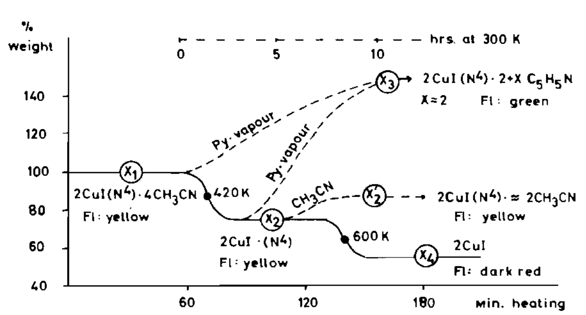

Figure 3. Thermal decomposition and re-absorption of vapours of $2CuI\cdot(CH_2)_6N_4\cdot 4CH_3CN$ with respective fluorescence colours (Fl). Py = pyridine, (N^4) = hexamethylenetetramine, X_1–X_4: samples taken for X-ray diffraction; $X_1 \neq X_2 \neq X_2' \neq X_4$; $X_2 = X_2'$.

vate molecules, and it is therefore obvious that they are to re-adsorb these solvating compounds from their vapour phase to a certain extent (Figure 2).

$3CuI\cdot(CH_2)_6N_4$, obtained by thermal decomposition of $3CuI\cdot(CH_2)_6N_4\cdot 2C_5H_5N$ is able to re-adsorb twice as much pyridine as it contained before, if it is kept in a pyridine atmosphere at room temperature for about 30 hr.

$2CuI\cdot(CH_2)_6N_4$, obtained by thermal decomposition of $2CuI\cdot(CH_2)_6N_4\cdot 4CH_3CN$, will re-adsorb approx. half of its former content, *e.g.* ≈2 mol of acetonitrile within 10 hr, if it is kept in an acetonitrile atmosphere at room temperature.

Pyridine, apparently having a greater donor number[9] than acetonitrile will also quickly replace acetonitrile in $2CuI\cdot(CH_2)_6N_4\cdot 4CH_3CN$ (Figure 3) within 10 hr at room temperature. During thermal decomposition the residues have different X-ray interferences from those of the respective starting compounds, but there is no difference in structure between the *blue* fluorescent $3CuI\cdot(CH_2)_6N_4\cdot 2C_5H_5N$ and the *green* fluorescent complex $3CuI\cdot(CH_2)_6N_4\cdot(2+x)C_5H_5N$; this instable adduct may be an inclusion compound or have additional molecules of pyridine occluded in the original structure. The complex $3CuI\cdot(CH_2)_6N_4\cdot 2C_5N_5N$ is moreover of some interest as it clearly shows phosphorescence after being excited by the 254 nm radiation at 77 K, the long wave 365 nm ultra violet light being uneffective. On heating $3CuI\cdot(CH_2)_6N_4\cdot 2C_5H_5N$ to 350–430 K, the brilliant blue fluorescence decreases eventually, but reappears after cooling the sample to room temperature.

This is not a case of fluorescence thermochromism but comes from a temporary breaking of copper–nitrogen bonds during heating.

Discussion

Thermochromism in the visible spectrum, *i.e.* a reversible change of colour in solids depending on temperature, is generally due to some change in structure (*e.g.* in $Ag_2(HgI_4)$). Therefore of course possible structural variations during cooling the fluorescent thermochromic compound from room temperature down to 77 K are of special interest.

However, there has been only one attempt to examine this, namely with the fluorescent and thermochromic 3-ethylpyridino-copper(I) iodide done by A. Simon[8]; in this case both Guinier diagrams at 300 and at 77 K proved to be identical.

This does not necessarily mean that atomic distances are not altered for certain atoms, thus changing or influencing the fluorescence colours, but X-ray investigations seem not to be applicable for obtaining an exact explanation of the phenomenon of fluorescence thermochromism itself.

After A. Pierre[6] was able to prepare the first monocrystals of a fluorescent and thermochromic compound, morpholino-copper(I) iodide (fl. orange at 300 K, red at 77 K), V. Schramm[7] succeeded in calculating its room temperature structure. The result is briefly that tetrameric clusters of (Cu_4I_4) are surrounded by four morpholino ligands, which are probably allowed to twist a little around their copper–nitrogen bonds, and this may be the reason for variation in fluorescence colour depending on thermal movements, whilst extremely short copper–copper distances (approx. 2.65 Å) are believed to be responsible for the fluorescence effect itself.

Similar tetrameric clusters have already been found at cuprous iodide complexes with trialkylphosphines and trialkylarsines[10], some of them having proved to be fluorescent and also thermochromic[6]. The essential question, why some complexes of copper(I) iodide with hexamethylenetetramine are thermochromic but others are not (Table I), cannot be answered exactly for structural data of these compounds are lacking. However, it should be possible to deduce some structural facts from chemical behaviour and other properties.

If one may suppose that the hexamethylenetetramine complexes have tetrameric copper iodide clusters such as had been found for the thermochromic morpholino copper iodide, those complexes which involve nitrogen bases (*e.g.* No 2 and 3 in Table I) could form a spongy framework structure, where not more than two copper atoms per Cu_4I_4 cluster are linked to nitrogen atoms, the others being coordinated to solvent molecules.

Thus the structure may be moveable enough to alter those atomic distances which induce fluorescence colours, even after the solvate molecules are subsequently evaporated.

All the other complexes in which each copper atom has at least 1.33 nitrogen functions available, are supposed to be of particularly tight structure, and there is perhaps not enough mobility in their lattice for thermochromism.

This framework hypothesis could possibly explain why copper iodide reacts with two different nitrogen bases (*e.g.* hexamethylenetetramine and pyridine) as well as with a sufficent surplus of hexamethylenetetramine to form non-thermochromic but brilliantly fluorescent compounds, and is also in conformity with the observation that these complexes are not only fluorescent, but possibly able to phosphoresce, if they have been previously excited at 77 K with 254 nm radiation.

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