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Thermochromic System of Halogen-Substituted Dinitrodiamminecopper(II). I. Formation, Transition, and Spectroscopy

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A series of compounds $[CuX_n(NO_2)_{2-n}(NH_3)_2]$, where X = Cl or Br, was obtained in a water–methanol–ethyl acetate solvent. These compounds exist in a purple form at low temperatures and in a green form at high temperatures, the temperature of transition becoming lower as the content of the chloride or bromide ion increases. This is also accompanied by a decrease in the heat of transition as shown by dta. Ir spectroscopy by use of ^{15}N and D substitution, as well as a preliminary X-ray study, has shown that the purple form contains N-coordinated NO_2, whereas the green form has an O-chelated O_2N group. The greater Weiss constant Θ of the purple form in the adaptation of $1/\chi_M$ to $(T + \Theta)/C$ is in conformity with the above conclusion.

Introduction

Dinitrodiamminecopper(II), $[Cu(NO_2)_2(NH_3)_2]$, was first prepared by Bassett, *et al.*,[1] by thermal decomposition of $[Cu(NH_3)_4](NO_2)_2$ under a vacuum below 100°. Tomlinson and Hathaway[2] reported that the compound prepared in this way exists in a green form at 65° and in a purple form below 35°.

While attempting to prepare the ammonium salt of $[Cu(NO_2)_5]^{3-}$, the authors obtained, instead of the desired substance, a series of purple and green crystalline substances which were $[Cu(NO_2)_2(NH_3)_2]$ and its derivatives in which a portion of the NO_2 groups was replaced by Cl or Br. This paper describes the condition of preparation, electronic and ir spectra, dta, X-ray studies, etc. of these compounds.

Experimental Section

Preparation of the Parent Compound $[Cu(NO_2)_2(NH_3)_2]$. A solution of 10.4 g (0.15 mol) of sodium nitrite in the least possible amount (around 30 ml) of water was added to 20 ml of water containing 4.8 g (0.02 mol) of copper(II) nitrate trihydrate and 6.4 g (0.08 mol) of ammonium nitrate, and at once was then added 100 ml of methanol. The solution was stirred for about 30 min and filtered, and to the filtrate was added 100 ml of ethyl acetate. Purple or almost black crystals of $[Cu(NO_2)_2(NH_3)_2]$ were deposited when the mixture was left standing for a few days at about 15°. The compound is unstable toward moist air, especially in a pulverized state.

The preparation could also be effected by using ammonium fluoride, ammonium iodide, ammonium thiocyanate, ammonium perchlorate, or ammonium sulfate instead of ammonium nitrate. As seen from the above description, the procedure is quite a simple one. Nevertheless, the condition of formation of the desired product seems to be limited to a narrow range of freedom. Thus use of too much sodium nitrite or too low temperatures contaminates the sample with sodium nitrate whereas insufficient sodium nitrite or ammonium salt as well as too high temperatures causes precipitation of greenish white basic copper salts. The precipitation of basic copper salts sometimes occurs due to an unknown cause, especially in summer seasons. This erratic nature of the formation can to some extent be overcome by use of ammonium nitrite instead of sodium nitrite and ammonium salts.

Preparation of $[CuX_n(NO_2)_{2-n}(NH_3)_2]$, X = Cl or Br. The procedure employed for the preparation of this series of compounds is analogous to that used for the preparation of $[Cu(NO_2)_2(NH_3)_2]$, but the *nitrate* ion was totally or partially replaced by equimolar amounts of the chloride or bromide ion. The value of *n* varies with the composition of the starting solution used in the preparation. The analytical values of such compounds prepared at various X:Cu ratios with [Cu] constant in the above directions are shown in Table I. The data clearly show that a part of the *nitrite* ion was replaced by the chloride or bromide ion.

Instrumentation. Infrared spectra in the range 4000–700 cm^{-1} were recorded with a Jasco IR-E infrared spectrophotometer and those in the range 700–250 cm^{-1} with a Hitachi EPI-L grating infrared spectrophotometer.

The electronic spectra of the solid compounds were measured by the reflectance technique using a Hitachi EPS-3T recording spectrophotometer with potassium sulfate as the reference.

Table I. Analytical Results of $[CuX_n(NO_2)_{2-n}(NH_3)_2]$ Crystallized from Solutions with Varying [X]/[Cu]

[Cl]/[Cu] in soln	Wt % in the Crystals: Cu	NH_3	NO_2	Cl	Molar ratio of Cl to Cu (=*n*)
		Calcd for *n* = 0			
	33.5	17.9	48.5	0	0
		Found			
0	33.5	17.5	48.8	0	0
0.3				1.05	(0.056)[a]
0.8				2.9	(0.15)
1.0	33.2	17.5	44.6	3.5	0.19
1.25				4.7	(0.25)
1.5				5.6	(0.30)
2.0	34.1	17.9	38.6	7.2	0.38
4.0	34.7	18.4	27.3	15.4	0.80
6.0	35.1	19.7	6.1	36.3	1.85
7.0	36.5			42.3	2.08
		Calcd for *n* = 2			
	37.7	20.2	0	42.1	2
[Br]/[Cu] in soln	Wt % in the crystals: Cu	N	H	Br	Molar ratio of Br to Cu (=*n*)
		Calcd for *n* = 0			
	33.5	29.6	3.17	0	0
		Found			
0.5		26.7	3.17	2.3	(0.055)
2.0		24.5	2.96	9.3	(0.23)
4.0		18.5	2.65	31.6	(0.87)
		Calcd for *n* = 2			
	24.7	10.9	2.33	62.1	2

[a] The numbers in parentheses were calculated from the content of X only, with the assumption of the above chemical formula.

X-Ray powder diffraction diagrams were obtained with a Rigaku SG-7 diffractometer, with the goniometer radius of 18 cm, using Cu Kα radiation (λ 0.1542 nm) filtered with a Ni foil, with the speed of rotation of 1°/min. Single-crystal photographic intensity data were collected with a Rion XP 1801 Weissenberg camera.

Differential thermal analyses were made using a Rigaku DTA 8001 instrument.

The magnetic measurements were performed using a Shimazu MB-2 magnetic balance with hexaamminechromium(III) chloride used as the reference.

Results

Color and Temperature. The compound containing no halide ion X (X = Cl, Br) gave purple crystals at room temperatures which turned green above about 30°. The color change is more easily seen in the pulverized state. The compounds containing 2.9 and 5.6 wt % of the chloride ion gave green crystals even

Table II. Result of Dta of $[CuX_n(NO_2)_{2-n}(NH_3)_2]$

Wt % of Cl	Molar ratio[a] of Cl to Cu (=*n*)	Transition temp, °C		Heat of transition, kJ/mol
		Ascending	Descending	
0	0	31–32	24–26	8.24
1.05	0.056	26, 17–18	17–18, 12–14	8.20
2.9	0.15	0–1	−12	5.82
3.5	0.19	−12 to −9.5	−25.5	4.69
4.7	0.25	−24 to −20	−35	3.68
5.6	0.30	−47 to −36	−54	2.68
7.2	0.38	No peak		
15.4	0.80	No peak		
36.3	1.85	No peak		

Wt % of Br	Molar ratio[a] of Br to Cu (=*n*)	Transition temp, °C		Heat of transition, kJ/mol
		Ascending	Descending	
2.3	0.055	17–18	7.5	7.99
9.3	0.23	−32 to −30	−52	3.47
31.6	0.87	No peak		

[a] See Table I.

at room temperatures which changed to purple ones at a Dry Ice temperature. The compounds containing more than 7.2 wt % of the chloride ion were green at room temperatures and did not undergo any color change at a liquid nitrogen temperature. The compound containing 1.05 wt % of the chloride ion was a mixture of the green and purple forms at room temperatures. The compounds containing 2.3 and 9.3 wt % of the bromide ion both gave green forms and changed to the purple forms at a Dry Ice temperature. The compound containing 31.6 wt % of the bromide ion was green at room temperatures and did not undergo any color change at a liquid nitrogen temperature.

Differential Thermal Analysis. The results of the dta of the compounds containing various amounts of the chloride or bromide ion are shown in Table II. The endothermic peak observed when the temperature is raised moves with the change of the chloride or bromide content in the compound and always lies at a higher temperature range than the exothermic peak observed when the temperature is lowered. This peak whose position varies with the chloride or bromide content is directly related to the change of color. Thus each compound is in the green form at higher temperatures than that of the peak position and in the purple form at lower temperatures than that of the peak position.

X-Ray Powder Diffraction. Some typical X-ray powder diffraction diagrams of the compounds of various chloride contents are shown in Figure 1. It is evident that the green and purple forms have different crystal structures. The diffraction diagrams of any powder samples of comparatively low chloride ion content in the green form are very similar to each other irrespective of the chloride ion content, except for a slight shift of each peak to higher angle with increasing chloride content in the compound proving that the size of the crystal lattice becomes smaller. The diffraction diagram of the compound of high Cl content, *e.g.*, 42.3 and 36.3 wt %, is distinctly different from those of the green and purple forms of lower chloride content and agrees with that of α-$[CuCl_2(NH_3)_2]$.[5] In some ranges of Cl content the sample has been shown to be a mixture of different types of crystals.

The situation is more or less similar in the case of samples containing bromide ions, though shrinkage of the lattice with increasing Br content was scarcely observed in this case. The types of the X-ray diffraction diagrams of the compounds of various chloride or bromide ion contents may be summarized in Table III.

Preliminary Crystal Structure Analysis. Green crystals of the formula $[CuCl_{0.17}(NO_2)_{1.83}(NH_3)_2]$ (mol wt 187.8) at room temperatures belong to the monoclinic system. The lattice parameters are a = 8.996 Å, b = 7.529 Å, c = 4.440 Å, and β = 104.4°. The unit cell volume is V = 291.3 Å^3. The density of the material, measured by a flotation technique, was found to be 2.24 g cm^{-3}. Assuming two formula units per cell, the calculated value is 2.14 g cm^{-3}. The space group is *Cm* or *C*2, probably *Cm*. Although a preliminary result of structural analysis using intensity data of 336 independent nonzero reflections obtained by Weissenberg equiinclination photography suggested trans coordination of two ammonia ligands and O chelation of one of the nitrite ions giving R = 0.12, the positions of the atoms of the other nitrite ion could not be determined because of unusual values of the anisotropic temperature factors of these atoms. This unhappy result may be due to the presence of chloride ion in the compound. An attempt to solve the structure by assuming a random distribution of the chloride ion at the nitrite positions has so far been unsuccessful.

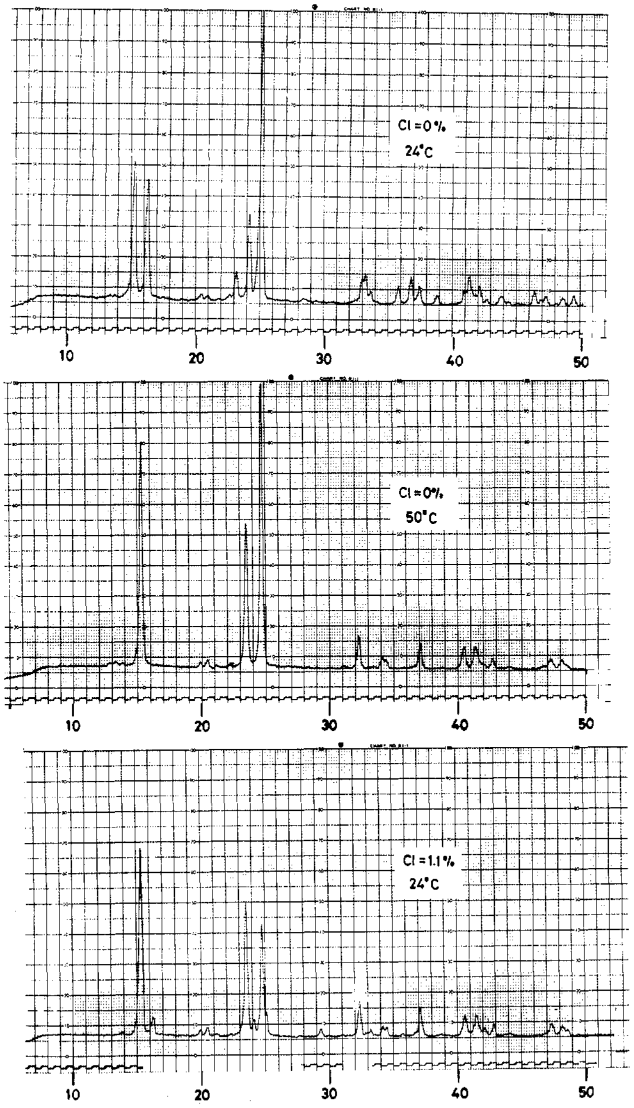

Figure 1. Some typical X-ray powder patterns of different forms of $[CuX_n(NO_2)_{2-n}(NH_3)_2]$. Abscissas: 2$\theta$ in degrees.

Electronic Spectra. The reflectance spectra of the compounds containing various chloride or bromide contents were recorded in the 14,000–30,000-cm^{-1} region, and the frequencies of the maxima in the $f(R_d) = (1 - R_d)^2/2R_d$ curve (which should correspond to the absorption maxima) are also given in Table III.

Infrared Spectra. The frequencies of the absorption bands in the ir spectra recorded in the 250–4000-cm^{-1} region are

Table III. Types of X-ray Powder Patterns of $[CuX_n(NO_2)_{2-n}(NH_3)_2]$ and Peak Positions in Their Electronic Spectra

		n^a	Purple form	Green form	α-$[CuCl_2$-$(NH_3)_2]$	$[CuBr_2$-$(NH_3)_2]$	Peak position, 10^3 cm^{-1}
Wt % of Cl	0 (24°)	0	A^b				18.6
	0 (50°)	0		A			16.4
	1.05	0.056	A	A			16.9
	2.9	0.15		A			15.9
	3.5	0.19		(A)^c			15.9
	5.6	0.30		(A)			15.9
	7.2	0.38		A			15.9
	16.0	0.82		A	A?		15.3
	36.3	1.85			A		14.7
	42.1	2			A		14.6
Wt % of Br	9.3	0.23		A			15.7
	31.6	0.87		A		A	14.7 24.8
	62.1	2				A	14.7 22

^{a} See Table I. ^{b} The symbol A indicates the appearance of the pattern characteristic of the form given in the headings. ^{c} (A) was inferred from data for lower and higher Cl contents.

Table IV. Peak Positions (cm^{-1}) in the Ir Spectra of the Different Forms of $[Cu(NO_2)_2(NH_3)_2]$

Purple form	3320	3250	3180	1620	1360	1330	1265	(1180 vw)	830	815	760	690	485	425
Green form	3320	3250	3180	1620	1380		1260	1180	845	820	730	690	483	
Purple form (deuterated)	2460	2360	2340	1185	1360	1330	980		830	815	575	525	458	425
Assignment	ν NH_3	ν NH_3	ν NH_3	δ NH_3	ν_{as} NO_2	ν_s $NO_2{}^a$	δ_s NH_3	ν_s O_2N^b	δ ONO	δ ONO	ρ NH_3	ρ_r NH_3	ν Cu–NH_3	ν Cu–NO_2

^{a} N coordination. ^{b} O chelation.

given in Table IV. Any sample in the violet form, *i.e.*, one below the transition temperature (including, of course, pure $[Cu(NO_2)_2(NH_3)_2]$ at room temperature), gave essentially the same ir spectrum irrespective of the chloride ion content, whereas one in the green form, *i.e.*, one above the transition temperature, gave another type of ir spectrum. The assignment of the bands due to the ammonia ligand was obvious from comparison with other ammine complexes. The single band at about 485 cm^{-1} observed both in the green form and the purple form is assigned as a Cu–NH_3 stretching mode because $[Cu(NO_2)_2(ND_3)_2]$ shows a corresponding band at the expected region of 460 cm^{-1}.

The assignment of vibrations due to NO_2 was made according to earlier workers.[3,4] The peak at 425 cm^{-1}, appearing only in the spectrum of the purple form, was assigned as the Cu–NO_2 stretching mode because it showed an expected shift to 415 cm^{-1} for the purple form of $[Cu(^{15}NO_2)_2(NH_3)_2]$. The above-mentioned Cu–NH_3 stretching vibration at 485 cm^{-1} naturally was not shifted by this substitution.

Magnetic Measurements. Magnetic measurements of compounds containing various amounts of chloride or bromide ion were performed at different temperatures over the range of 77–366 K. In this region the inverse values of the molar susceptibilities of the compounds show linear dependence on the absolute temperatures. As examples, two such plots are shown in Figures 2 and 3. There is a break in the plot around the transition temperature. The value of Θ in the adaptation of $1/\chi_M$ to $3k(T + \Theta)/N\mu_{eff}^2\beta^2$ is small in the high-temperature form, whereas it is about 20 K in the low-temperature form. The effective Bohr magneton number μ_{eff}, as defined in the above formula, has nearly constant values of 1.73–1.80 in both forms.

Discussion

Because both the color change and the peak of the dta were observed even in the compound containing no halide ion, the transition should not be the one related to the halide ion directly. However, the fact that this change occurred at lower temperatures and the transition energy decreased with increasing chloride or bromide content shows that the green form is stabilized in the presence of the chloride or bromide ion. The data in Table II show that such stabilization is more effectively operative in the case of the substitution by bromide ion as compared with the substitution by about the same molar ratio of the chloride ion.

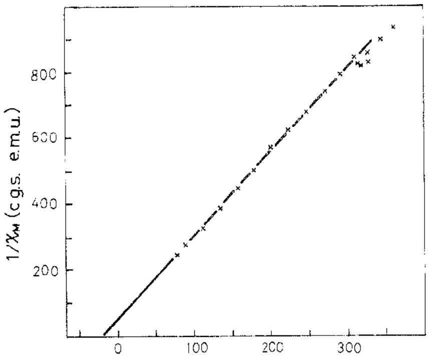

Figure 2. Plot of the reciprocal values of the molar susceptibility of $[Cu(NO_2)_2(NH_3)_2]$ against the absolute temperature.

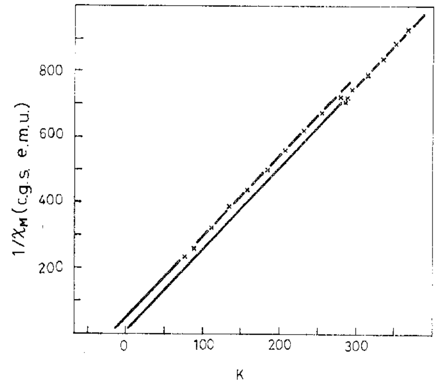

Figure 3. Plot of the reciprocal values of the molar susceptibility of $[CuCl_{0.15}(NO_2)_{1.85}(NH_3)_2]$ against the absolute temperature.

The X-ray diffraction diagram of the compound containing 1.05 wt % of the chloride ion mainly consisted of the characteristic pattern of the green form superimposed on those of the purple form present in lower abundance. This result is consistent with that of dta: while the temperature is raised, *e.g.*, such a sample gave a large peak at a lower temperature