



Fig. 1. ORTEP drawing (Johnson, 1976) of $(C_5H_5)_3Yb^{III}$. Dashed line: trace of closest-packed zigzag chain in the lattice.

Table 3. Parameters indicative of variable packing of $(C_5H_5)_3Ln^{III}$ molecules

Ln	$(Ln \cdots C')_{min}^*$ (Å)	$(Ln \cdots Ln')_{min}^*$ (Å)	$Ln \cdots Ln' \cdots Ln''$ (°)	D_x (g cm ⁻³)
Er	3.137 3.190	5.806 5.934	114.3 114.9	2.038
Tm	3.243 3.334	5.891 6.040	114.5 113.8	2.045
Yb	4.139	6.739	72.7	2.027
Lu	2.519 (2.654)	6.163	107.7	2.100

* Shortest possible intermolecular distance.

$Yb^{III}(N_2C_4H_4)_{1/2}$ [2.68(1) Å; Baker & Raymond (1977)] and $(C_5H_5)_3Lu^{III}.THF$ [2.69(4) Å; Ni *et al.* (1985)].

other hand, further support for the assumption of weak 'chemical' interactions between each Tm^{III} (or Er^{III}) ion and one distinct ring C atom of an adjacent $(C_5H_5)_3Ln$ molecule.

The structural non-equivalence of (solution-) crystallized $(C_5H_5)_3Yb^{III}$ and (vacuum-) sublimed $(C_5H_5)_3Tm^{III}$ may be compared with the recently reported (Lamberts, Lueken & Elsenhans, 1986) dimorphism of $[(C_5H_5)_2Gd^{III}(\mu_2-Br)]_2$ which consists either of isolated molecules (sublimation temperature ~ 403 K; $D_x = 2.289$ g cm⁻³) or of infinite chains of μ_3 -Br-bridged dimers (sublimation temperature ~ 423 K; $D_x = 2.392$ g cm⁻³).

The displacement of the Yb^{III} ion from the plane of the three C_5H_5 ring centres (0.050 Å) is notably smaller than the corresponding quantity for $Ln = Tm$ or Er (*ca* 0.3 Å) and also that in $\{[(CH_3)_3Si]_2N\}_3Yb^{III}$ (*ca* 0.4 Å; Eller, Bradley, Hursthouse & Meek, 1977). Hence, $(C_5H_5)_3Yb^{III}$ belongs to the still-rare group of condensed LnX_3 systems of almost ideal pseudo- D_{3h} microsymmetry. Expectedly (Fischer & Li, 1985), the mean $Yb-C$ distance of 2.639 Å in the base-free molecule is slightly shorter than the corresponding distance in the pseudotetrahedral molecules $(C_5H_5)_3-$

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Structure of Thermochromic Crystals of Benzimidazolium Tetrachlorocuprate(II) Hydrate

BY M. BUKOWSKA-STRZYŻEWSKA AND J. SKOWERANDA

Institute of General Chemistry, Technical University, 36 Żwirki, 90 924 Łódź, Poland

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Abstract. $2C_7H_7N^+.CuCl_4^{2-}.H_2O$, $M_r = 461.7$, monoclinic, $P2_1/c$, $a = 16.040$ (3), $b = 4.243$ (1), $c = 27.501$ (6) Å, $\beta = 104.78$ (4)°, $V = 1809.7$ (8) Å³, Z

$= 4$, $D_x = 1.690$ (1) Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.85$ mm⁻¹, $F(000) = 932$, $T = 293$ K, final $R = 0.038$, $wR = 0.042$ for 2806 reflections [$I > 3\sigma(I)$]. The

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structure consists of polymeric $[\text{CuCl}_4]_{\infty}^-$ and $[\text{CuCl}_2(\text{H}_2\text{O})_2]_{\infty}$ chains, cationic columns formed by stacking of planar benzimidazolium ions and chloride anions linked by $\text{N}-\text{H}\cdots\text{Cl}$ and $\cdots\text{Cl}\cdots\text{H}-\text{O}-\text{H}\cdots\text{Cl}\cdots$ hydrogen bonds. A system of hydrogen bonds $\text{N}-\text{H}\cdots\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}$, $\text{N}-\text{H}\cdots\text{Cl}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{Cl}$ links

the polymeric chains with the cationic columns. The Cu atoms are six-coordinated with two very long Cu-Cl bonds, 3.154 (1) and 3.330 (1) Å, and four short Cu-Cl(H₂O) bonds, 2.272 (1), 2.275 (1), 2.294 (1) and 1.954 (2) Å, respectively.

Introduction. Interest in the structure of copper(II) halide complexes results from their large structural variability and their significance for many disciplines from inorganic biochemistry (Solomon, Hare, Dodey, Dawson, Stephens & Gray, 1980; Wherland & Gray, 1977) through catalysis (Davies & El-Sayed, 1983) to solid-state physics (Willett & Landee, 1981). The extremely diverse and complex crystal chemistry of copper(II) halides is due to the presence of an active Jahn-Teller effect in the d^9 electronic system and the relative flatness of the potential surfaces for many distortions (Lohr & Lipscomb, 1963). For CuX_4^{2-} species the coordination geometries range from nearly tetrahedral with a superimposed D_{2d} distortion, to a completely planar D_{4h} species.

This paper gives the results of the structural investigation of $(\text{C}_7\text{H}_7\text{N}_2)_2\text{CuCl}_4\cdot\text{H}_2\text{O}$, a new reversible thermochromic halide complex.

Experimental. The title compound was prepared by dissolving 1 g of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ in 25 ml of water and 4 ml of concentrated HCl; 2 g of benzimidazole dissolved in 25 ml of warm water were then added. The green solution was left to evaporate slowly. After a few days, pale-green crystals were obtained, in the shape of long (a few centimetres) very thin needles. The previously obtained and examined stable dark-brown crystals of $(\text{C}_7\text{H}_7\text{N}_2)\text{CuCl}_3$ were formed in an ethanol solution, with a benzimidazole to copper molar ratio of 1:1 (Bukowska-Strzyżewska, Tosik, Głowiak & Wnęk, 1985). Chemical analysis of the pale-green crystals did not solve the ambiguity between the anhydrous and monohydrated formula. It was only the X-ray diffraction study that made it possible to determine the correct composition $(\text{C}_7\text{H}_7\text{N}_2)_2\text{CuCl}_4\cdot\text{H}_2\text{O}$. At a temperature of 316 K, these crystals quickly change their colour to bright orange. At room temperature, the orange crystals slowly take on the green colour again. The rate of the reverse change of colour from orange to green depends not only on the temperature but also on the air humidity. At room temperature the orange crystals retain their colour from within a few days to a few weeks. Below 273 K, the change of colour occurs within a few hours. We have not found a loss of the

Table 1. Atomic coordinates ($\times 10^5$ for Cu and Cl atoms; $\times 10^4$ for C, N and O atoms) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^2$ for Cu and Cl atoms, $\times 10$ for C, N and O atoms) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
Cu(1)	0	0	0	370 (4)
Cu(2)	50000	0	50000	376 (4)
Cl(1)	-14254 (5)	2351 (24)	-199 (3)	378 (6)
Cl(2)	3268 (6)	33814 (30)	6729 (4)	471 (8)
Cl(3)	40085 (6)	-36721 (27)	50742 (4)	433 (7)
Cl(4)	45267 (6)	50719 (26)	35073 (3)	408 (6)
O	4496 (2)	112 (6)	4274 (1)	34 (2)
N(1)	1444 (2)	187 (8)	4115 (1)	42 (3)
N(2)	2661 (2)	1377 (9)	3970 (1)	53 (3)
N(3)	7568 (2)	-83 (8)	4092 (1)	38 (2)
N(4)	6281 (2)	-1297 (8)	3677 (1)	40 (2)
C(1)	1264 (2)	2131 (9)	3700 (1)	33 (3)
C(2)	489 (2)	3273 (9)	3408 (1)	39 (3)
C(3)	538 (3)	5158 (10)	3013 (1)	47 (3)
C(4)	1313 (3)	5835 (11)	2905 (2)	56 (4)
C(5)	2085 (3)	4748 (11)	3195 (2)	56 (4)
C(6)	2039 (2)	2879 (9)	3600 (1)	40 (3)
C(7)	2279 (3)	-167 (11)	4265 (2)	56 (4)
C(8)	7419 (2)	1530 (9)	3642 (1)	33 (3)
C(9)	7931 (2)	3560 (10)	3450 (2)	45 (3)
C(10)	7570 (3)	4701 (10)	2978 (2)	58 (4)
C(11)	6745 (3)	3884 (11)	2704 (1)	57 (4)
C(12)	6241 (3)	1900 (10)	2891 (1)	47 (3)
C(13)	6593 (2)	720 (8)	3373 (1)	34 (3)
C(14)	6885 (2)	-1751 (10)	4098 (1)	42 (3)

water molecule during the rapid colour change at 316 K. However, the long (several days) exposure of the orange crystals over CaCl_2 even at room temperature caused the loss of the water molecule without decomposition of the crystal structure. The diffractometric phase analysis indicated the different structures of the green and orange crystals.

The pale-green crystals were found to be monoclinic $P2_1/c$ (systematic absences: $k = 2n+1$ for $0k0$, $l = 2n+1$ for $h0l$) with the needle axis parallel to **b**. Crystal $0.3 \times 0.5 \times 0.2$ mm. Syntex $P2_1$ diffractometer. 15 reflections with θ between 22 and 27° used for determination of lattice parameters. Two intensity and orientation control reflections measured every 50 reflections showed no significant drift in intensity. Scan rate $2-29.3^\circ \text{ min}^{-1}$ depending on intensity. $2 \leq 2\theta \leq 50^\circ$, $h0-20$, $k0-5$, $l-34-29$; 3792 unique reflections measured, 2806 data with $I \geq 3\sigma(I)$. 226 parameters refined. Syntex (1976) *XTL/XTLE Structure Determination System*. Lp and empirical absorption correction; transmission factors 0.707-1.19. Structure solved from a Patterson map. H atoms located at expected positions, only H(1w) and H(2w) from the difference electron density map. Positional and anisotropic thermal parameters of non-H atoms refined on F with weights based on counting statistics. The coordinates of the H atoms and their Debye-Waller temperature parameters ($B = 5.0 \text{ Å}^2$) were kept fixed. $R = 0.038$, $wR = 0.042$, $w = 1/\sigma^2(F)$, $S = 3.64$. Max.

Table 2. *Geometry of the hydrogen bonds (e.s.d.'s in parentheses)*

It is assumed that e.s.d.'s for H atoms in unrefined positions are ten times those of the atoms to which are attached.

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$\angle D-H\cdots A$ (°)
N(1)—H(5)⋯Cl(1 ⁱ)	1.00 (3)	2.61 (3)	3.263 (3)	123 (3)
N(1)—H(5)⋯Cl(2 ⁱⁱ)		2.21 (3)	3.137 (3)	153 (3)
N(3)—H(12)⋯Cl(2 ⁱⁱⁱ)		2.63 (3)	3.336 (3)	129 (3)
N(3)—H(12)⋯Cl(1 ⁱⁱⁱ)		2.77 (3)	3.368 (3)	122 (4)
N(3)—H(12)⋯Cl(1 ^{iv})	1.00 (3)	2.62 (3)	3.285 (3)	121 (3)
N(4)—H(14)⋯Cl(4 ^v)	1.00 (3)	2.15 (3)	3.137 (3)	170 (3)
N(2)—H(7)⋯O	1.00 (3)	1.96 (3)	2.897 (4)	155 (4)
O—H(1w)⋯Cl(4)	0.84 (2)	2.21 (3)	2.988 (3)	156 (4)
O—H(2w)⋯Cl(4 ^v)	0.81 (2)	2.29 (3)	3.012 (3)	149 (3)
C(7)—H(6)⋯Cl(3)	1.00 (3)	2.54 (3)	3.422 (5)	147 (4)
C(7)—H(6)⋯Cl(1 ^v)		2.86 (4)	3.382 (5)	113 (3)
C(14)—H(13)⋯Cl(3 ^v)	1.00 (3)	2.63 (3)	3.550 (5)	156 (3)

Symmetry code: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1+x, -\frac{1}{2}-y, \frac{1}{2}+z$; (iv) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x, -1+y, z$; (vi) $1-x, -1-y, 1-z$.

puckering of the aromatic rings under the influence of hydrogen bonds. Benzimidazolium cations form stacked columns extending along the y axis. Short van der Waals contacts within both crystallographically independent columns are shown in Fig. 2. Four cationic columns surround each polymeric chain, forming a net of hydrogen bonds. Their geometry with calculated H-atom positions is illustrated in Table 2. The H(5) atom forms inequivalent bifurcated hydrogen bonds N(1)—H(5)⋯Cl(1ⁱ) of 2.21 (3) and 2.61 (3) Å. The

H(12) atom is in the field of three Cl⁻ ions with distances H(12)—Cl(2ⁱⁱⁱ) 2.63 (3), H(12)—Cl(1ⁱⁱⁱ) 2.77 (3) and H(12)—Cl(1^{iv}) 2.62 (3) Å. The shortest H⋯Cl hydrogen bond is 2.15 (3) Å. C—H⋯Cl hydrogen bonds of 2.54 (3), 2.63 (3) and 2.86 (4) Å were observed. Symmetry codes are given in Table 2.

In order to explain the mechanism of reversible thermochromic properties of the crystals, a study of the structure of the orange form is planned.

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Structure of Disodium Ethylenebisdithiocarbamate Hexahydrate

BY VIKTOR VRÁBEL, ŠTEFAN GERGELY, JÁN LOKAJ, ELEONÓRA KELLÖ AND JÁN GARAJ

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Jánska 1, 812 37 Bratislava, Czechoslovakia

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Abstract. $\text{Na}_2[\text{S}_2\text{CNH}(\text{CH}_2)_2\text{HNCS}_2] \cdot 6\text{H}_2\text{O}$, $M_r = 364.4$, triclinic, $P\bar{1}$, $a = 5.781$ (4), $b = 7.237$ (7), $c = 10.063$ (12) Å, $\alpha = 88.50$ (9), $\beta = 81.60$ (8), $\gamma = 74.24$ (7)°, $V = 400.8$ (7) Å³, $Z = 1$, $D_m = 1.51$, $D_x = 1.51$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.6$ mm⁻¹, $F(000) = 190$, $T = 295$ K, $R = 0.038$ for 1308 observed reflections. The geometry about Na⁺ is distorted octahedral, consisting of five water molecules and one S atom from the organic ligand. Four bidentate water molecules form bridging units between two Na⁺ cations on both sides of the organic anion and thus

form an infinite chain structure. The ethylenebis-dithiocarbamate ion acts as a bidentate ligand; each S atom is an acceptor of three hydrogen bonds.

Introduction. In complexes containing the $R_2\text{NCS}_2^-$ ligand, the geometry of the $>\text{NCS}_2$ moiety is dependent on the substituents R_2 as well as the actual coordination environment. It has previously been shown that for sodium dithiocarbamates, $\text{Na}[\text{S}_2\text{CNR}_2] \cdot n\text{H}_2\text{O}$, there is a strong correlation between the ligand bite and the bulkiness of the substituents R (Ymén, 1983). Although