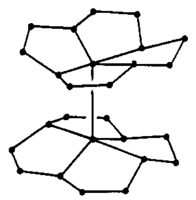
The implication is that less P–N π bonding is present for axial bonds compared to equatorial bonds.[19] The presence of relatively rigid five-membered rings, fused to the diazadiphosphetidine ring, and the tendency of the axial nitrogen atoms toward planarity may be responsible to some extent for the widening of the equatorial NA1–P1–NB4 angle to 133.8 (1)° and the displacement of the structure toward a square pyramid (40.4% based on unit vectors). In the case of the cis-facial structures VIII, this displacement corresponded to a structure near the midpoint between the two idealized pentacoordinated geometries.[3]

It is interesting that each of the five-membered rings tends to be coplanar with its attached phenyl ring. The dihedral angles between these pairs of planes are 7.5, 10.4, and 17.9° for phenyl rings attached at CA3, CC3, and CB3, respectively (Table D). This agrees with the double-bond character implied by the length of the C–C bond, averaging 1.470 (4) Å, at the point of attachment of the phenyl groups. However, bond distance data for both the fluoro and chloro derivatives of VIII[3] are very similar to those for IX reported here, and in these structures, the dihedral angles between planes of the five-membered rings and attached phenyl groups range from 22 to 26°.[3] Possibly, crystal-packing forces for the cis-facial structures VIII lead to the out-of-plane rotation of the phenyl groups (with respect to the five-membered rings) without appreciable loss of C–C π bonding.

The partial facial-meridonal structure for the tricyclic arrangement around P1 of IX may be compared with the completely cyclized bis(cyclenphosphorane) $(C_8H_{16}N_4P)_2$ containing two N_4 macrocycles with saturated five-membered rings (XI). In this structure,[20] the P–N axial bonds are 1.782 (2) Å, and the P–N equatorial bonds, 1.694 (2) Å.



XI

The ^{31}P NMR data for IX indicate that the solid-state structure is retained in solution. The presence of an equilibrium mixture of two diastereomers, each containing a five-coordinate and four-coordinate phosphorus atom, is supported by the observance of the two AB spin systems with appropriate chemical shifts for these coordination numbers. Assuming the retention of the basic ring triazaphosphole structure of X, it is reasonable to conclude that the pentacoordinated phosphorus atom is the spirocyclic center containing the fused five-membered rings.

Acknowledgment. The support of this work by a grant from the National Institutes of Health (GM 21466) is gratefully acknowledged. We also express appreciation to the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. VIIIb, 63148-50-5; IX, 82808-35-3; X, 52713-97-0.

Supplementary Material Available: Tables A–D, compilations of anisotropic thermal parameters, refined parameters for hydrogen atoms, remaining bond lengths and angles, and deviations from selected least-squares mean planes for IX and a listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

---

(18) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*, 85–86.

(19) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

(20) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955; *Inorg. Chem.* **1981**, *20*, 3378.

Contribution from the Consiglio Nazionale delle Ricerche of Italy, Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy, Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffrattometrica, University of Parma, 43100 Parma, Italy, and Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy

N-(2-Ammonioethyl)morpholinium Tetrachlorocuprates(II). The First Instance of Two Forms, One Green and One Yellow, Both Stable at Room Temperature

L. P. BATTAGLIA,[1a] A. BONAMARTINI CORRADI,[1a] G. MARCOTRIGIANO,[1b] L. MENABUE,[1c]
and G. C. PELLACANI*[1c]

Received February 12, 1982

Crystals of the green form of the title compound are monoclinic, space group $I2/a$, with a = 15.934 (3) Å, b = 13.023 (1) Å, c = 14.069 (3) Å, β = 118.89 (1)°, and Z = 8. Crystals of the yellow form are monoclinic, space group $P2_1/a$, with a = 15.909 (3) Å, b = 12.420 (3) Å, c = 6.355 (1) Å, β = 98.77 (5)°, and Z = 4. The crystal structures were determined by three-dimensional X-ray diffraction and refined to R = 0.047 and 0.045 for the green and yellow forms, respectively. In the green crystals two crystallographically independent $[CuCl_4]^{2-}$ anions are present, one of them with a flattened-tetrahedral geometry and the other square planar for symmetry requirements. In the yellow form only $[CuCl_4]^{2-}$ distorted-tetrahedral ions are present. In both modifications, the anions form hydrogen bonds with the *N*-(2-ammonioethyl)morpholinium cation, with stronger bonds being present in the green modification. The spectroscopic and magnetic properties of the complexes are explained in the light of their known crystal structures.

Introduction

The great interest in the tetrachlorocuprates(II) stems from the fact that they show a great variety of coordination numbers and geometries[2,3] and, in some cases, a discontinuous reversible thermochromic behavior.

---

(1) (a) University of Parma. (b) University of Bari. (c) University of Modena.

(2) Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93 and references cited therein.

(3) Bloomquist, D. R.; Willett, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 2615 and references cited therein.

0020-1669/82/1321-3919$01.25/0

This last phenomenon in $[CuCl_4]^{2-}$ salts consists of a color change at a certain temperature value as a consequence of a transformation of the coordination geometry. In general the green to yellow color change is the result of relaxation of anion geometry from a sterically crowded square-planar arrangement of ligands to a less constrained distorted-tetrahedral configuration[4] favored by a weakening of the hydrogen-bonding network as a result of the increasing disorder due to thermal motion.

While there are some spectroscopic evidences of this,[5-7] structural evidence is only reported for the bis(methylphenethylammonium) tetrachlorocuprate(II) system, which at 25 °C is greeen and contains square-coplanar $[CuCl_4]^{2-}$ ions and at 80 °C is yellow and contains flattened-tetrahedral $[CuCl_4]^{2-}$ ions,[8] and for the bis(isopropylammonium) tetrachlorocuprate(II) system, the room-temperature structure of which consists of ribbons of five- and six-coordinate copper(II) ions,[9] while the structure of the high-temperature phase turns out to contain distorted-tetrahedral $[CuCl_4]^{2-}$ ions.[10] In all cases, however, the two forms interconvert at a well-defined temperature value, called the "temperature transition".

In this paper we report the first instance of a compound, [*N*-(2-ammonioethyl)morpholinium tetrachlorocuprate(II), which exists in two forms, one green and one yellow, both stable at room temperature. The compounds were characterized by means of structural, spectroscopic, and magnetic measurements.

Experimental Section

All reagents were reagent grade and used as received.

Preparation of the Complexes. The yellow form, $[N\text{-}(2\text{-amet})\text{-}mfH_2]CuCl_4$, was prepared by mixing copper(II) chloride dihydrate and the amine (1:1 molar ratio) in concentrated hydrochloric acid. Anal. Calcd for $C_6H_{16}CuN_2OCl_4$: C, 21.33; H, 4.78; N, 8.30. Found: C, 21.39; H, 4.83; N, 8.28.

The green form was prepared by mixing copper(II) chloride dihydrate and the amine (1:1 molar ratio) in concentrated hydrochloric acid, then adding ethanol until incipient precipitation, and then letting the solution stand for several hours. Anal. Calcd for $C_6H_{16}CuN_2OCl_4$: C, 21.33; H, 4.78; N, 8.30. Found: C, 21.43; H, 4.79; N, 8.21.

Physical Measurements. The electronic spectra of the solid compounds were recorded at room temperature as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra as Nujol mulls on KBr pellets as support (4000–250 cm^{-1}) were recorded with a Perkin-Elmer 180 spectrophotometer. The room-temperature magnetic moments were measured with the Gouy method by using $Ni(en)_3S_2O_3$ as calibration standard and correcting for diamagnetism with the appropriate Pascal constants. Differential scanning calorimetric analysis (DSC) was performed with a Perkin-Elmer DSC-1 instrument in the 30–200 °C temperature range.

X-ray Data Collection. In both compounds, preliminary cell dimensions were obtained from rotation and Weissenberg photographs; subsequently these values were refined by least-squares using 2θ values of 15 high-angle reflections accurately measured on an "on-line" single-crystal automated Siemens AED diffractometer with Mo Kα radiation (λ = 0.710 688 Å) for the green form and Cu Kα radiation (λ = 1.541 78 Å) for the yellow form. The refined cell constants and other relevant crystal data are given in Table I. Crystals were mounted with their [010] and [100] axes along the φ axis of the diffractometer for the green and yellow forms, respectively, and intensity data were collected at a takeoff angle of 3° with use of the Nb-filtered Mo Kα radiation for the former and Ni-filtered Cu Kα radiation for the latter. The moving-counter–moving-crystal scan technique was employed with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). After every 20 reflections one reflection was measured as a check of alignment and of crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during the data collection. The intensities of 2580 independent reflections were measured for the green compound and 2371 for the yellow one; of these 1435 and 2165, respectively, having $I > 2\sigma(I)$ were considered as observed and used in the structural analyses ($\sigma(I)$ = [(total counts) + (0.005(intensity))]$^{1/2}$). After the usual data reduction, the intensities were put on an absolute scale by least squares. The correction for absorption was applied only to the data of the yellow compound, its transmission factors ranging from 0.09 to 0.53. For the green crystals the $\mu\bar{r}$ value is very low (0.21); therefore, with assumption of cylindrical shape for the crystals, the absorption correction factor A^* is unchanged in the 3–26θ range (1.40).

Table I. Summary of Crystal Data Collection

	I (green form)	II (yellow form)
mol formula	$C_6H_{16}Cl_4CuN_2O$	$C_6H_{16}Cl_4CuN_2O$
mol wt	337.5	337.5
a, Å	15.934 (3)	15.909 (3)
b, Å	13.023 (1)	12.420 (3)
c, Å	14.069 (3)	6.355 (1)
β, deg	118.89 (3)	98.77 (5)
V, Å^3	2556 (1)	1241 (1)
Z	8	4
d_{obsd} (by flotation), g cm^{-3}	1.74	1.78
d_{calcd}, g cm^{-3}	1.75	1.80
space group^a	*I*2/*a*	*P*2$_1$/*a*
cryst dimens, mm	0.10 × 0.23 × 0.59	0.07 × 0.26 × 0.88
radiation	Mo Kα ($\bar{\lambda}$ = 0.710 688 Å)	Cu Kα ($\bar{\lambda}$ = 1.541 78 Å)
abs coeff, cm^{-1}	25.3	104.1
F(000)	1368	684
unique data used ($I > 2\sigma(I)$)	1453	2165
no. of variables	129	127
% *R* ($R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$)	4.7	4.45
% R_w ($R_w = [\Sigma w\lvert\Delta F\rvert^2/\Sigma wF_o^2]^{1/2}$)	4.8	5.6

^{a} The standard lattices can be obtained by applying the following transformation matrices: for the green form, from *I*2/*a* to *C*2/*c*, $|-1, 0, -1|0, -1, 0|0, 0, 1|$ (a = 14.236, b = 13.023, c = 14.069 Å; β = 121.0°); for the yellow form, from *P*2$_1$/*a* to *P*2$_1$/*c*, $|0, 0, 1|0, 1, 0|1, 0, 0|$ (a = 6.355, b = 12.420, c = 15.909 Å; β = 98.77°).

Structure Analysis and Refinement. Both structures were solved by the heavy-atom method and refined by full-matrix least squares with anisotropic thermal parameters for Cu, Cl, O, N, and C. The hydrogen atoms were located in ΔF maps and included in the calculations of the final structure factors. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = k/[\sigma^2(F_o) + g(F_o)^2]$, where k = 1 and g = 0.00574 for the green crystal and k = 0.539 and g = 0.00917 for the yellow crystal. The final *R*'s were 0.047 and 0.045 for the green and yellow forms, respectively. The atomic scattering factors were taken from ref 11. The effects of anomalous dispersion were corrected by including the values of $\Delta f'$ and $\Delta f''$ in the calculation for Cu and Cl for both compounds. The fractional atomic coordinates are listed in Table II. A listing of observed and calculated structure factors for the reflections used in the structural analyses with thermal parameters is available in the supplementary material. All the calculations were performed on the Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord Orientale, Bologna, Italy, using the SHELX system.[12]

Results and Discussion

Description of the Structures. Bond distances and angles for both forms are quoted in Table III; the hydrogen-bonding

---

(4) Roberts, S. A.; Bloomquist, D. R.; Willett, R. D.; Dodgen, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 2603 and references cited therein.

(5) Willett, R. D.; Haugen, J. A.; Lebsack, J.; Morrey, J. *Inorg. Chem.* **1974**, *13*, 2510.

(6) Willett, R. D.; Ferraro, J. R.; Choca, M. *Inorg. Chem.* **1974**, *13*, 2919.

(7) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1976**, *15*, 2333.

(8) Harlow, R. L.; Wells, W. J., III; Watt, J. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2106.

(9) Anderson, D. N.; Willett, R. D. *Inorg. Chim. Acta* **1974**, *8*, 167.

(10) Bloomquist, D. R.; Willett, R. D.; Dodgen, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 2610.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(12) Sheldrick, G. M. "A Program for Crystal Structure Determination"; University Chemical Laboratory: Cambridge, England, 1976.

Table II. Fractional Atomic Coordinates for Cu, Cl, O, N, and C with Esd's in Parentheses

	x	y	z
	(a) Green Form		
Cu(1)	0	0	0
Cu(2)	0.2500	0.3898 (1)	0
Cl(1)	0.1438 (1)	−0.0399 (2)	0.0181 (1)
Cl(2)	0.0710 (1)	0.0332 (1)	0.1843 (1)
Cl(3)	0.2191 (1)	0.2717 (1)	0.0981 (1)
Cl(4)	0.3568 (2)	0.5036 (2)	−0.0010 (2)
O	−0.1381 (4)	0.1758 (4)	0.2699 (5)
N(1)	0.2010 (4)	0.4461 (5)	0.2516 (4)
N(2)	−0.0209 (3)	0.3211 (4)	0.2331 (4)
C(1)	0.1236 (5)	0.4264 (6)	0.2786 (6)
C(2)	0.0542 (4)	0.3485 (5)	0.2018 (5)
C(3)	0.0167 (6)	0.2594 (6)	0.3360 (6)
C(4)	−0.0616 (6)	0.2293 (7)	0.3605 (7)
C(5)	−0.1776 (5)	0.2387 (7)	0.1758 (7)
C(6)	−0.1020 (5)	0.2650 (6)	0.1424 (6)
	(b) Yellow Form		
Cu	−0.1057 (0)	0.1871 (0)	−0.0059 (1)
Cl(1)	−0.1362 (1)	0.2097 (1)	−0.3617 (2)
Cl(2)	0.0203 (1)	0.2746 (1)	0.0403 (2)
Cl(3)	−0.2348 (1)	0.2247 (1)	0.0769 (2)
Cl(4)	−0.0693 (1)	0.0441 (1)	0.2034 (2)
O	0.4059 (2)	−0.0668 (2)	0.4556 (6)
N(1)	0.0567 (2)	0.1946 (3)	0.5460 (6)
N(2)	0.2616 (2)	0.0763 (2)	0.4205 (5)
C(1)	0.1496 (2)	0.1812 (3)	0.5586 (9)
C(2)	0.1678 (2)	0.0957 (3)	0.4026 (6)
C(3)	0.2807 (3)	0.0065 (4)	0.2412 (7)
C(4)	0.3752 (3)	−0.0134 (4)	0.2598 (9)
C(5)	0.3932 (3)	0.0018 (4)	0.6282 (8)
C(6)	0.2991 (3)	0.0247 (4)	0.6288 (7)

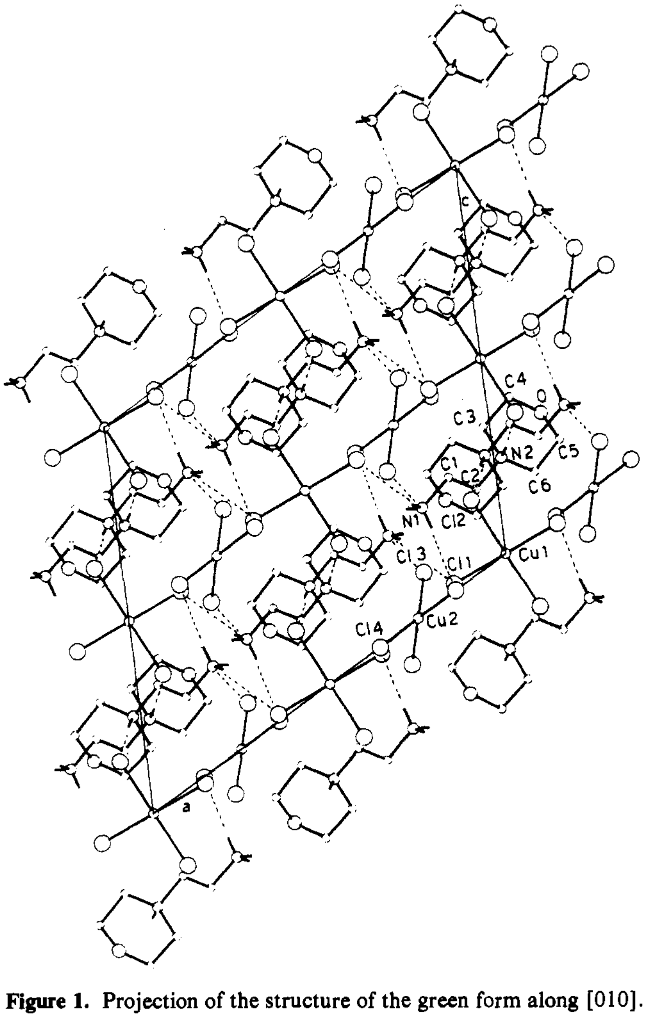


Figure 1. Projection of the structure of the green form along [010].

Table III. Bond Distances (Å) and Angles (Deg) with Esd's in Parentheses for the $[CuCl_4]^{2-}$ Anions[a]

(a) Green Form			
Cu(1)–Cl(1)	2.240 (1)	Cu(2)–Cl(3)	2.269 (1)
Cu(1)–Cl(2)	2.314 (1)	Cu(2)–Cl(4)	2.266 (3)
Cl(1)-Cu(1)–Cl(2)	89.80 (5)	Cl(3)-Cu(2)-Cl(4)^{i}	93.17 (2)
Cl(3)–Cu(2)–Cl(4)	146.24 (8)	Cl(4)-Cu(2)-Cl(4)^{i}	97.88 (2)
Cl(3)–Cu(2)–Cl(3)^{i}	95.11 (1)		
(b) Yellow Form			
Cu–Cl(1)	2.256 (1)	Cu–Cl(3)	2.245 (1)
Cu–Cl(2)	2.259 (1)	Cu–Cl(4)	2.241 (1)
Cl(1)–Cu–Cl(2)	96.97 (6)	Cl(2)-Cu–Cl(3)	133.98 (5)
Cl(1)–Cu–Cl(3)	98.30 (7)	Cl(2)–Cu–Cl(4)	99.22 (6)
Cl(1)-Cu–Cl(4)	133.61 (5)	Cl(3)–Cu–Cl(4)	100.87 (7)

[a] The superscript i denotes the symmetry operation $^1/_2 - x, y, -z$.

Table IV. Hydrogen Bonding Distances (Å) and Angles (Deg)

(a) Green Form[a]			
N(1)···Cl(4)^{i}	3.271 (6)	N(1)···Cl(3)^{ii}	3.397 (6)
Cl(4)^{i}···H(1)	2.43	Cl(3)^{ii}···H(3)	2.64
N(1)–H(1)	0.84	N(1)–H(3)	0.93
N(1)···Cl(1)^{ii}	3.219 (5)	N(2)···Cl(2)^{iii}	3.242 (5)
Cl(1)^{ii}···H(2)	2.55	Cl(2)^{iii}···H(4)	2.35
N(1)–H(2)	0.93	N(2)–H(4)	0.89
N(1)–H(1)···Cl(4)^{i}	167	N(1)–H(3)···Cl(3)^{ii}	138
N(1)–H(2)···Cl(1)^{ii}	128	N(2)–H(4)···Cl(2)^{iii}	174
(b) Yellow Form			
N(1)···Cl(2)	3.329 (4)	N(2)···Cl(3)^{iii}	3.304 (3)
Cl(2)···H(1)	2.35	Cl(3)^{iii}···H(4)	2.61
N(1)–H(1)	1.08	N(2)–H(4)	0.95
N(1)···O^{i}	3.023 (5)	N(2)···Cl(1)^{iv}	3.307 (3)
O^{i}···H(2)	2.37	Cl(1)^{iv}···H(4)	2.54
N(1)–H(2)	0.97	N(2)–H(4)	0.95
N(1)···Cl(4)^{ii}	3.357 (4)		
Cl(4)^{ii}···H(3)	2.53		
N(1)–H(3)	0.96		
N(1)–H(1)···Cl(2)	150	N(2)–H(4)···Cl(3)^{iii}	130
N(1)–H(2)···O^{i}	124	N(2)–H(4)···Cl(1)^{iv}	138
N(1)–H(3)···Cl(4)^{ii}	145		

[a] The superscripts denote the following symmetry operations: i = $^1/_2 - x, y, -z$; ii = $^1/_2 - x, ^1/_2 - y, ^1/_2 - z$; iii = $-x, ^1/_2 + y, ^1/_2 - z$. [b] The superscripts denote the following symmetry operations: i = $^1/_2 - x, ^1/_2 + y, 1 - z$; ii = $-x, y, 1 - z$; iii = $^1/_2 + x, ^1/_2 - y, z$; iv = $^1/_2 + x, ^1/_2 - y, 1 + z$.

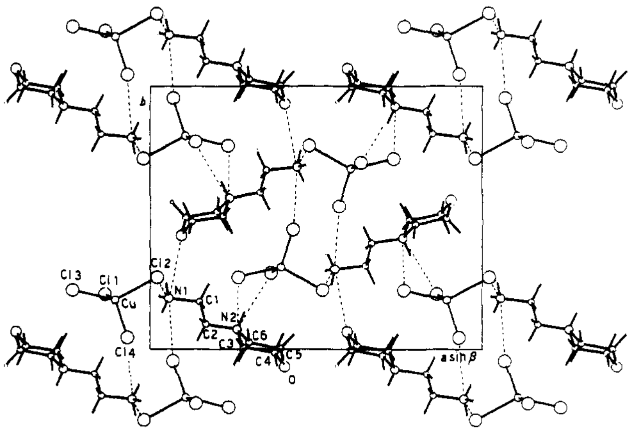


Figure 2. Projection of the structure of the yellow form along [001].

distances are depicted in Figures 1 and 2 and quoted in Table IV.

Both structures consist of N-(2-ammonioethyl)morpholinium dications and discrete $[CuCl_4]^{2-}$ anions. The most relevant differences for the structures of the green and yellow form are

Table V. Room-Temperature Magnetic (μ_B) and Spectroscopic (cm^{-1}) Results for the Solid Complexes

	green form	yellow form
μ_{eff}	1.85	1.93
d-d bands	9300	6250
	11 560	9620
	14 290 sh	
	16 400	
charge-transfer bands	22 220 sh	21 980 sh
	25 640	24 510

the different geometries of the $[CuCl_4]^{2-}$ chromophore in the two cases. In the green crystals, two crystallographically independent $[CuCl_4]^{2-}$ anions are present, the former, lying at the origin of the cell, square planar for symmetry requirements and the latter, on the twofold axis, exhibiting a very flattened tetrahedral geometry. In the green form, the Cu–Cl distances in the square-planar $[CuCl_4]^{2-}$ anion are significantly different (2.240 (1), 2.314 (1) Å), the former being comparable to the 2.248-Å value found in the $(PhCH_2CH_2NMeH_2)_2CuCl_4$[8] low-temperature form, in which square-planar $[CuCl_4]^{2-}$ anions are present. The Cu–Cl distances in the tetrahedral unit (green form) are very similar (2.269 (1), 2.266 (1) Å) and comparable to those found in other flattened-tetrahedral $[CuCl_4]^{2-}$ anions.[13,14] The deformation from tetrahedral geometry can be expressed by the dihedral angle $\mathrm{Cl(3)CuCl(3)^i \wedge Cl(4)CuCl(4)^i}$ ($i = {}^1/_2 - x, y, -z$) of 45.8°, similar to the 49.5° value found in $(C_{13}H_{19}N_2OS)_2CuCl_4$[15] and intermediate between tetrahedral (90°) and square-planar (0°) configuration. As illustrated in Figure 1 and Table IV, packing is mainly determined by Cl···HN hydrogen bonds, the shortest of them involving the square-planar $[CuCl_4]^{2-}$ anion.

The influence of hydrogen bonds on Cu–Cl distances is confirmed on observing that the Cu–Cl(2) (2.314 (1) Å) longest bond length corresponds to the Cl(2)···H shortest distance. In the yellow form, the CuCl distances (2.241–2.259 Å) are quite similar and are within the range previously found for other $[CuCl_4]^{2-}$ anions having similar tetrahedral distortion. The distortion from the tetrahedral geometry in this compound, measured by the $\mathrm{Cl(1)CuCl(3) \wedge Cl(2)CuCl(4)}$ dihedral angle (63.0°), is smaller than that found in the green compound but similar to the 63.7° value found in $[(C_2H_5)_3NH]_2CuCl_4$.[16] The smaller deformation of the tetrahedron in the yellow form can be explained by observing the Cl···HN hydrogen bond values, which are similar (3.31–3.36 Å) and weaker than those found in the green compound; one of them can be considered as a bifurcated hydrogen bond. Moreover, in this compound the morpholine oxygen atom also participates in the packing, forming an O···HN hydrogen bond.

In both compounds the morpholine moiety exhibits the "chair" conformation, as indicated by the puckering parameters:[17] $q_2 = 0.042$ Å, $q_3 = 0.568$ Å, $\varphi_2 = 235°$, $Q = 0.57$ Å (green form); $q_2 = 0.031$ Å, $q_3 = 0.589$ Å, $\varphi_2 = 162°$, $Q = 0.59$ Å (yellow form). The distances of N and C atoms from the main plane through the carbon atoms are −0.65 and +0.66 Å, respectively, for the green form and +0.67 and −0.69 Å for the yellow form. The kind of conformation and bond distances and angles in the morpholine ring are usual in the coordinated and uncoordinated morpholine molecule.[18]

Differential Scanning Calorimetric, Magnetic, and Spectroscopic Results. DSC measurements indicate that both compounds are stable in the temperature range between 30 °C and their melting points (190 °C).

The room-temperature magnetic moments (Table V) of the compounds are typical of "magnetically dilute" systems.[19]

The room-temperature electronic spectrum of the yellow form (Table V) agrees very well with those normally found for similarly flattened tetrahedral $[CuCl_4]^{2-}$ (D_{2d} symmetry) anions,[13,20-22] while that of the green form (Table V) is complicated by the simultaneous presence of two unequally flattened $[CuCl_4]^{2-}$ units in the cell. However, in the light of its known crystal structure, by using the correlation between the d–d band maximum transition and the degree of tetrahedral distortion, expressed as a diehedral angle, previously reported,[13] we were able to find the theoretically predictable d–d band maximum for $[CuCl_4]^{2-}$ anions with experimental dihedral angles of 45.8 and 0° at 11 410 and 16 260 cm^{-1}, respectively. Thus the bands at 9300 and 11 560 cm^{-1} can be reliably assigned to the lower distorted-tetrahedral $[CuCl_4]^{2-}$ unit and the other two to the square-planar $[CuCl_4]^{2-}$ unit, present in the green form.

Comparison with the band intensities and positions of other complexes containing square-planar $[CuCl_4]^{2-}$ anions, which present three distinct peaks in the ranges 11 500–12 500, 13 600–13 840, and 16 100–16 530 cm^{-1}[8,23] strongly supports our tentative assignments.

Comparison of the infrared spectra of the two forms shows that there are no appreciable differences in band shapes and positions of the cation, even though it is differently involved in hydrogen bonding in the crystal packing of the two compounds, which confirms the insufficiency of this technique to point out these types of differences.

Acknowledgment. The authors are grateful to Professor M. Nardelli for helpful discussion and to the Centro Strumenti dell'Università di Modena for the recording of the IR spectra.

Registry No. I, 82638-66-2; II, 82621-22-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances and angles for the cation, fractional atomic coordinates for hydrogen atoms, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

---

(13) Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1979**, *18*, 148 and references cited therein.

(14) Antolini, L.; Menabue, L.; Pellacani, G. C.; Saladini, M.; Marcotrigiano, G.; Porzio, W. *J. Chem. Soc., Dalton Trans.* **1981**, 1753.

(15) Bonamartini, A.; Nardelli, M.; Palmieri, C.; Pelizzi, C. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1775.

(16) Lamotte-Brasseur, J.; Dupont, L.; Dideberg, O. *Acta Crystallogr., Sect. B* **1973**, *B29*, 241.

(17) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

(18) Battaglia, L. P.; Bonamartini Corradi, A.; Grasselli Palmieri, C. *Cryst. Struct. Commun.* **1973**, *3*, 523.

(19) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

(20) Lamotte-Brasseur, J. *Acta Crystallogr., Sect. A* **1974**, *30*, 487.

(21) Hatfield, W. E.; Piper, T. S. *Inorg. Chem.* **1964**, *3*, 841.

(22) Furlani, C.; Cervone, E.; Calzona, F.; Baldanza, B. *Theor. Chim. Acta* **1967**, *7*, 375.

(23) Hitchman, M. A. *J. Chem. Soc., Chem. Commun.* **1979**, *973*.