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Distortion Isomerism in a Thiocyanate-Bridged Copper(II) Dimer. X-ray Structure of β -Bis(μ -thiocyanato-*N,S*)bis[bis(5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine)(thiocyanato-*N*)copper(II)] and Comparison of Its Spectral and Structural Properties with Those of Other Copper(II) 5,7-Dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine Thiocyanates[†]

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Copper(II) thiocyanate and 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine ($C_7H_8N_4$, dmtp) form three different complexes: two isomers of composition $[Cu(NCS)_2(dmtp)_2]_2$ and the hydrated species $Cu(NCS)_2(dmtp)_2 \cdot H_2O$. The structure of the β isomer of $[Cu(NCS)_2(dmtp)_2]_2$ has been determined by single-crystal X-ray diffraction techniques. The compound is monoclinic, $P2_1/n$, with $a = 10.928$ (3) Å, $b = 14.709$ (3) Å, $c = 12.804$ (3) Å, $\beta = 95.31$ (2)°, $Z = 4$, $d_{\text{obsd}} = 1.535$ Mg·m⁻³, and $d_{\text{calcd}} = 1.54$ Mg·m⁻³. The final R_w value is 0.034. The compound is a centrosymmetric dimer. Each asymmetric unit is linked to another one via two NCS bridges between the copper atoms. Each copper atom is surrounded by five donor atoms: two N atoms of two monodentate dmtp ligands (N(3)), one N of a nonbridging NCS ion, and an N and an S atom of the two bridging NCS ions. β - $[Cu(NCS)_2(dmtp)_2]_2$ appears to be a distortion isomer of the earlier reported α compound. The structural differences of the two isomers are correlated with their IR, UV, and ESR spectra and magnetic susceptibilities. Spectral properties of the hydrate $Cu(NCS)_2(dmtp)_2 \cdot H_2O$ are discussed as well.

Introduction

The study of the interactions between metal ions and fragments of nucleic acids is of extreme interest, because it has been found that such interactions are vital for all kinds of biological processes.¹ 5,7-Dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine, hereafter abbreviated as dmtp, has been shown to be a versatile ligand for many transition-metal ions.^{2,3} As an azapurine it mimics the N(9) coordination type of the purines in its N(3) coordination mode. Moreover, its potential ability to coordinate in more than one way, e.g. by linking metals together via N(3) and N(4), allows the study of metal-metal interactions. Therefore, we have used this ligand to study its coordinating properties to transition metals, especially to copper. Figure 1 gives its structural formula and IUPAC atom-numbering system compared to the biochemical atom numbering of purine. In a previous communication³ we have briefly mentioned the existence of three coordination compounds between dmtp and copper(II) thiocyanate and described the preparation and the structure of the green α - $[Cu(NCS)_2(dmtp)_2]_2$. In this paper we report the preparation of the brown β isomer from a hydrate of composition $Cu(NCS)_2(dmtp)_2 \cdot H_2O$. To investigate the structural differences, we have undertaken a study of the spectroscopic properties of the three compounds and studied the X-ray structure of the β isomer. No crystals suitable for X-ray analysis could be obtained for the hydrated product.

Experimental Section

Preparations. The metal salts for the preparations were reagent grade and were used without further purification. The ligand dmtp was prepared according to the method of Bülow and Haas⁴ from reagent grade pentane-2,5-dione and 3-amino-1,2,4-triazole. Copper(II) thiocyanate (2 mmol, 0.360 g), freshly prepared from copper(II) nitrate and ammonium thiocyanate, was added with stirring to a solution of dmtp (4 mmol, 0.593 g) in water (20 mL). A bright green precipitate was recovered after filtering, washing with water, and drying in air. Anal. Calcd for $Cu(NCS)_2(dmtp)_2 \cdot H_2O$: C, 38.90; H, 3.67; N, 2.835; Cu, 12.80. Found: C, 39.02; H, 3.69; N, 28.5; Cu, 13.0. When, however, the product was left in the mother liquor for several days, the product dissolved slowly and dark brown crystals were deposited. These crystals are easily separated from any Cu-

Table I. Diffraction Data for β - $[Cu(NCS)_2(dmtp)_2]_2$

space group	$P2_1/n$
lattice constants	
a , Å	10.928 (3)
b , Å	14.709 (3)
c , Å	12.804 (3)
β , deg	95.31 (2)
Z	4
cryst dimens, mm	$0.40 \times 0.25 \times 0.25$
θ range, deg	2-24
$F(000)$	966
no. of measd reflns	3401
no. of indep reflns	3213
no. of significant reflns ($I > 2\sigma(I)$)	2492
final R (R_w)	0.025 (0.034)
d_{obsd} , Mg·m ⁻³	1.535 (10)
d_{calcd} , Mg·m ⁻³	1.54 (1)

(NCS)₂(dmtp)₂·H₂O left by decantation. After filtering, washing, and drying the crystals were analyzed. Anal. Calcd for $[Cu(NCS)_2(dmtp)_2]_2$: C, 40.37; H, 3.39; N, 29.42; Cu, 13.35. Found: C, 40.26; H, 3.35; N, 29.2; Cu, 13.6. The green α - $[Cu(NCS)_2(dmtp)_2]_2$ was prepared as described before.³

Ligand field measurements. Ligand field spectra were taken on a Beckman DK2-A UV-vis-near-IR spectrophotometer using the diffuse-reflectance technique with MgO as reference. Infrared spectra were recorded on a Perkin-Elmer Model 580B IR spectrophotometer as Nujol mulls between KRS-5 (Tl(Br,I)) and polyethylene (below 400 cm⁻¹) and as CsCl disks. The ESR powder spectra were recorded on a Varian E-3 spectrometer at 9.5 GHz and on a Varian E-112 at 35 GHz. Magnetic susceptibility data were obtained in the temperature range 4-70 K on a PAR Model 150A vibrating-sample magnetometer using CoHg(SCN)₄ as a reference compound.

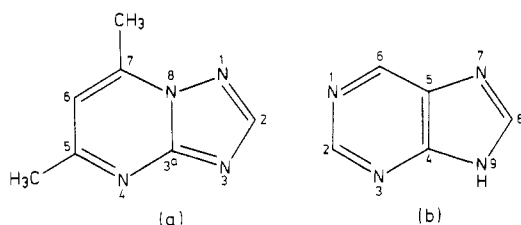
Structure Determination. A rhombic dodecahedral single crystal of β - $[Cu(NCS)_2(dmtp)_2]_2$ ($C_{32}H_{32}Cu_2N_{20}S_4$) was selected and mounted on an Enraf-Nonius DAD-4 four-circle diffractometer; Mo K α radiation ($\lambda = 0.71073$ Å), monochromated by graphite, was used

[†] Dedicated to the memory of Prof. Dr. J. Gazo, who died on Feb 15, 1983.

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Table II. Positional Parameters (for Cu(1) and S(7), $\times 10^5$; for N(2) to C(41), $\times 10^4$; for H(12) to H(413), $\times 10^3$) and Isotropic Thermal Factors for the Non-Hydrogen Atoms of β -[Cu(NCS)₂(dmp)₂]₂

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} , Å ²		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} , Å ²
Cu(1)	74317 (3)	716 (2)	48479 (2)	2.56 (1)	C(36)	9319 (3)	2107 (2)	1522 (2)	3.87 (8)
S(7)	66219 (6)	-12762 (5)	56081 (6)	3.37 (2)	C(37)	8257 (3)	1569 (2)	1531 (2)	3.50 (7)
N(2)	8258 (2)	289 (2)	6230 (2)	3.95 (7)	N(38)	7965 (2)	1136 (1)	2385 (2)	3.26 (6)
C(3)	8499 (3)	191 (2)	7115 (2)	3.75 (8)	C(39)	8751 (2)	1235 (2)	3239 (2)	2.69 (6)
S(4)	8894 (1)	60 (1)	8362 (1)	6.97 (4)	C(40)	11284 (3)	2741 (3)	2487 (3)	5.10 (11)
N(5)	4101 (2)	-1027 (2)	5019 (2)	3.39 (6)	C(41)	7392 (4)	1462 (3)	562 (3)	5.12 (12)
C(6)	5147 (2)	-1124 (2)	5244 (2)	2.79 (7)	H(12)	509 (2)	29 (2)	304 (2)	
N(11)	6739 (2)	-350 (1)	3434 (1)	2.75 (6)	H(16)	848 (3)	-213 (2)	73 (2)	
C(12)	5722 (3)	-96 (2)	2814 (2)	3.59 (8)	H(32)	994 (2)	110 (2)	544 (2)	
N(13)	5647 (2)	-390 (2)	1831 (2)	3.66 (6)	H(36)	947 (3)	235 (2)	84 (2)	
N(14)	6713 (2)	-886 (1)	1832 (2)	2.93 (6)	H(201)	536 (4)	-148 (3)	4 (3)	
C(15)	7116 (3)	-1352 (2)	1006 (2)	3.52 (8)	H(202)	628 (4)	-73 (3)	-33 (3)	
C(16)	8177 (3)	-1813 (2)	1241 (2)	4.30 (9)	H(203)	661 (3)	-164 (2)	-45 (3)	
C(17)	8805 (3)	-1792 (2)	2254 (2)	3.79 (8)	H(211)	1038 (4)	-219 (3)	317 (4)	
N(18)	8413 (2)	-1313 (1)	3031 (2)	3.08 (6)	H(212)	986 (5)	-286 (4)	239 (4)	
C(19)	7363 (2)	-863 (2)	2800 (2)	2.69 (7)	H(213)	1044 (5)	-242 (5)	179 (5)	
C(20)	6358 (4)	-1303 (3)	-15 (3)	5.23 (11)	H(401)	1141 (3)	304 (2)	187 (3)	
C(21)	9955 (4)	-2333 (3)	2501 (4)	5.91 (13)	H(402)	1193 (3)	235 (3)	265 (3)	
N(31)	8702 (2)	880 (1)	4203 (2)	2.61 (6)	H(403)	1124 (4)	325 (3)	313 (4)	
C(32)	9734 (2)	1214 (2)	4744 (2)	2.98 (7)	H(411)	674 (3)	108 (2)	60 (3)	
N(33)	10418 (2)	1751 (2)	4230 (2)	3.27 (6)	H(412)	707 (4)	207 (3)	34 (3)	
N(34)	9785 (2)	1763 (1)	3256 (2)	2.75 (6)	H(413)	790 (4)	124 (3)	-2 (3)	
C(35)	10113 (2)	2211 (2)	2387 (2)	3.43 (7)					

**Figure 1.** (a) IUPAC numbering scheme of dmp. (b) Commonly used biochemical numbering of purine.

to determine the unit cell parameters and the space group as well as to measure the reflection intensities at room temperature. The crystal and diffraction data are listed in Table I. The data were corrected for Lorentz and polarization effects. Absorption correction was necessary ($\mu = 13.3 \text{ cm}^{-1}$). After reduction of the intensities to structure factors a Wilson plot was calculated, from which starting values were obtained for the scaling parameter and the overall isotropic thermal parameter. The experimental density was determined in a mixture of 1,2-dibromoethane and trichloromethane. Scattering factors were taken from ref 5. All calculations were carried out on the Leiden University computers (IBM 370/158 and Amdahl V7B) using a set of computer programs locally written or modified by E. W. Rutten-Keulemans and Dr. R. A. G. de Graaff. The function minimized during the least-squares refinement was $\sum w(\Delta F)^2$, with $\Delta F = |F_o| - |F_c|$ and $w = \sigma_F^{-2}$. Reliability indices referred to are $R = \sum |\Delta F|/|F_o|$ and $R_w = [\sum w(\Delta F)^2 / \sum w|F_o|^2]^{1/2}$. The positions of 22 of the 29 non-hydrogen atoms were located using the program MULTAN.⁶ Three cycles of isotropic refinement followed by a difference Fourier synthesis yielded the positions of the other non-hydrogens. Another three cycles of refinement, with anisotropic temperature parameters, yielded $R = 0.05$, and the positions of all atoms led to $R = 0.025$ ($R_w = 0.034$). In Table II, the positional parameters are given together with the isotropic *B* values for the non-hydrogen atoms. The corresponding labeling of the atoms is given in Figure 2. The anisotropic thermal parameters for the non-hydrogens and a list of structure factors are available as supplementary material.⁷

Results and Discussion

Description of the Molecular Structure of the β Isomer. The structure of the β isomer is depicted in Figure 2 together with

the atomic labeling system used. Table III lists relevant bond distances and bond angles. During the process of the structure analysis it turned out that the molecular structure of the β isomer differed only slightly from that of the α isomer. A close look reveals that the structures differ in the extent to which they are distorted from a regular coordination geometry, here a square pyramid. Gazo has proposed the name *distortion isomerism* for this type.^{8,9} The basic structures of both compounds are schematically depicted in Figure 3. Both isomers are considered to have basically a square-pyramidal coordination in which one of the two bridging NCS groups coordinates axially. For the α isomer it is the S atom that is axial; for the β isomer it is the N atom. This difference is reflected in differences in metal-ligand distances: α isomer, $\text{Cu-S}_{\text{ax}} = 2.87 \text{ \AA}$, $\text{Cu-N}_{\text{eq}} = 1.95 \text{ \AA}$; β -isomer, $\text{Cu-S}_{\text{eq}} = 2.413 \text{ \AA}$, $\text{Cu-N}_{\text{ax}} = 2.205 \text{ \AA}$. Therefore, these compounds can equally well be called *linkage isomers*. If one regards these compounds as dimers of square-planar copper complexes, dimerization has occurred through bridging of NCS via the axial positions on the copper ions. The α isomer then is the dimer of $(\text{dmp})_2\text{Cu}(\text{NCS})_2$, whereas the β isomer is a dimer of $(\text{dmp})_2\text{Cu}(\text{NCS})(\text{SCN})$. In Table IV some relevant distances and bond angles of both isomers are compared with those of some other known copper(II)-thiocyanate systems.¹⁰⁻¹⁴ The copper-thiocyanate distances in both isomers clearly reflect the nature of the bond: Cu-N or Cu-S, and axial or equatorial. There seems to be little effect of terminal vs. bridging NCS groups. The Cu-S_{ax} bond length in the α isomer is still significantly shorter than the sum of the van der Waals radii of copper and sulfur (3.4 \AA ¹⁵). The Cu-SCN distance in the β compound, however, is relatively short compared to other Cu-SCN distances.¹⁶ This originates from the fact that

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(7) Supplementary material.

Table III. Bond Distances (Å) and Angles (deg) in β -[Cu(NCS)₂(dmtp)₂]₂

Cu(1)-N(2)	1.937 (2)	C(12)-H(12)	0.96 (3)	C(20)-H(203)	0.81 (4)	C(35)-C(40)	1.494 (4)
Cu(1)-S(7)	2.4125 (7)	N(13)-N(14)	1.374 (3)	C(21)-H(211)	0.96 (5)	C(36)-C(37)	1.405 (4)
Cu(1)-N(11)	1.995 (2)	N(14)-C(15)	1.367 (3)	C(21)-H(212)	0.80 (6)	C(36)-H(36)	0.98 (3)
Cu(1)-N(31)	2.058 (2)	N(14)-C(19)	1.371 (3)	C(21)-H(213)	1.10 (6)	C(37)-N(38)	1.330 (3)
Cu(1)-N(5')	2.205 (2)	C(15)-C(16)	1.353 (4)	N(31)-C(32)	1.360 (3)	C(37)-C(41)	1.498 (4)
N(2)-C(3)	1.149 (4)	C(15)-C(20)	1.483 (5)	N(31)-C(39)	1.346 (3)	N(38)-C(39)	1.335 (3)
C(3)-S(4)	1.627 (3)	C(16)-C(17)	1.410 (4)	C(32)-N(33)	1.306 (3)	C(40)-H(401)	0.93 (4)
N(5)-C(6)	1.161 (3)	C(17)-N(18)	1.322 (3)	C(32)-H(32)	0.92 (2)	C(40)-H(402)	0.92 (4)
C(6)-S(7)	1.652 (3)	C(17)-C(21)	1.497 (5)	N(33)-N(34)	1.369 (3)	C(40)-H(403)	1.12 (4)
N(11)-C(12)	1.357 (3)	N(18)-C(19)	1.334 (3)	N(34)-C(35)	1.369 (3)	C(41)-H(411)	0.91 (4)
N(11)-C(19)	1.340 (3)	C(20)-H(201)	1.13 (4)	N(34)-C(39)	1.369 (3)	C(41)-H(412)	1.00 (5)
C(12)-N(13)	1.326 (3)	C(20)-H(202)	0.93 (4)	C(35)-C(36)	1.351 (4)	C(41)-H(413)	1.02 (4)
N(2)-Cu(1)-N(11)	170.3 (1)	N(13)-N(14)-C(15)	126.8 (2)	H(202)-C(20)-H(203)	106 (3)	C(35)-C(36)-H(36)	123 (2)
N(2)-Cu(1)-N(31)	89.8 (1)	N(13)-N(14)-C(19)	110.9 (2)	C(17)-C(21)-H(211)	114 (3)	C(37)-C(36)-H(36)	115 (2)
N(2)-Cu(1)-N(5')	96.7 (1)	C(15)-N(14)-C(19)	122.3 (2)	C(17)-C(21)-H(212)	113 (4)	C(36)-C(37)-N(38)	122.5 (3)
N(2)-Cu(1)-S(7)	85.7 (1)	N(14)-C(15)-C(16)	114.2 (3)	C(17)-C(21)-H(213)	110 (3)	C(36)-C(37)-C(41)	120.7 (3)
S(7)-Cu(1)-N(11)	89.3 (1)	N(14)-C(15)-C(20)	117.7 (3)	H(211)-C(21)-H(212)	115 (5)	N(38)-C(37)-C(41)	116.8 (3)
S(7)-Cu(1)-N(31)	157.3 (1)	C(16)-C(15)-C(20)	128.2 (3)	H(211)-C(21)-H(213)	122 (4)	C(37)-N(38)-C(39)	115.8 (2)
S(7)-Cu(1)-N(5')	100.5 (1)	C(15)-C(16)-C(17)	121.9 (3)	H(212)-C(21)-H(213)	78 (5)	N(31)-C(39)-N(34)	108.0 (2)
N(11)-Cu(1)-N(31)	91.6 (1)	C(15)-C(16)-H(16)	118 (2)	Cu(1)-N(31)-C(32)	124.2 (2)	N(31)-C(39)-N(38)	129.1 (2)
N(11)-Cu(1)-N(5')	92.4 (1)	C(17)-C(16)-H(16)	120 (2)	Cu(1)-N(31)-C(39)	132.7 (2)	N(34)-C(39)-N(38)	122.9 (2)
N(31)-Cu(1)-N(5')	102.0 (1)	C(16)-C(17)-N(18)	122.7 (3)	C(32)-N(31)-C(39)	103.0 (2)	C(35)-C(40)-H(401)	112 (2)
Cu(1)-N(5')-C(6')	142.8 (2)	C(16)-C(17)-C(21)	120.7 (3)	N(31)-C(32)-N(33)	116.6 (2)	C(35)-C(40)-H(402)	109 (2)
Cu(1)-N(2)-C(3)	157.8 (2)	N(18)-C(17)-C(21)	116.6 (3)	N(31)-C(32)-H(32)	124 (2)	C(35)-C(40)-H(403)	109 (2)
N(2)-C(3)-S(4)	177.9 (3)	C(17)-N(18)-C(19)	115.4 (2)	N(33)-C(32)-H(32)	120 (2)	H(401)-C(40)-H(402)	109 (3)
N(5)-C(6)-S(7)	177.8 (2)	N(11)-C(19)-N(14)	108.2 (2)	C(32)-N(33)-N(34)	101.7 (2)	H(401)-C(40)-H(403)	109 (3)
Cu(1)-S(7)-C(6)	99.2 (2)	N(11)-C(19)-N(18)	128.4 (2)	N(33)-N(34)-C(35)	126.8 (2)	H(402)-C(40)-H(403)	110 (3)
Cu(1)-N(11)-C(12)	131.8 (2)	N(14)-C(19)-N(18)	123.5 (2)	N(33)-N(34)-C(39)	110.7 (2)	C(37)-C(41)-H(411)	117 (2)
Cu(1)-N(11)-C(19)	123.6 (2)	C(15)-C(20)-H(201)	113 (2)	C(35)-N(34)-C(39)	122.5 (2)	C(37)-C(41)-H(412)	109 (3)
C(12)-N(11)-C(19)	103.6 (2)	C(15)-C(20)-H(202)	116 (2)	N(34)-C(35)-C(36)	114.6 (2)	C(37)-C(41)-H(413)	107 (2)
N(11)-C(12)-N(13)	116.2 (3)	C(15)-C(20)-H(203)	113 (3)	N(34)-C(35)-C(40)	117.9 (3)	H(411)-C(41)-H(412)	109 (3)
N(11)-C(12)-H(12)	124 (2)	H(201)-C(20)-H(202)	101 (3)	C(36)-C(35)-C(40)	127.5 (3)	H(411)-C(41)-H(413)	109 (3)
N(13)-C(12)-H(12)	119 (2)	H(201)-C(20)-H(203)	107 (3)	C(35)-C(36)-C(37)	121.7 (3)	H(412)-C(41)-H(413)	107 (3)
C(12)-N(13)-N(14)	101.2 (2)						

Table IV. Comparison of Copper-Thiocyanate Distances (Å)^b

	ref	Cu-NCS(eq)	Cu-NCS(ax)	Cu-SCN(eq)	Cu-SCN(ax)
α -[Cu(NCS) ₂ (dmtp) ₂] ₂	3	1.954 (9) T 1.953 (8) B			2.886 (4) B
β -[Cu(NCS) ₂ (dmtp) ₂] ₂	<i>a</i>	1.937 (2) T	2.205 (2) B	2.413 (1) B	
Cu(NCS) ₂ ·(2-NH ₃ Et) ₂ NH	10	1.97 T	2.26 T		
Cu(en) ₂ Hg(SCN) ₂	11		2.58 B		
Cu(SCN)(OC ₂ H ₄ NMe ₂)	12				2.884 (2) B 3.073 (2) B
[Cu(trien)SCN](NCS)					2.607 (2) T
Cu(py) ₂ (NCS) ₂	14	1.94 (2) B			3.04 (2) B

^a This work. ^b Abbreviations: T = terminal, B = bridging, eq = equatorial, ax = axial.

in this compound the Cu-SCN bond is in an equatorial position, which is uncommon for copper(II)-thiocyanate complexes.^{16,17} The molecular geometry of the dmtp ligands is within standard deviation identical with that in the α isomer and in other dmtp complexes.^{2,3} The dimeric units are held together in the lattice by van der Waals forces. No stacking of the heterocyclic rings is observed.

Spectral Characterization. In view of the foregoing, the question arises whether or not the hydrated compound is also a dimer. Its ESR spectrum, in contrast to the spectra for the α and β isomers, shows a signal that is attributed to a mononuclear copper(II) species (vide infra). The infrared spectra of the compounds further afford information about the structure of the hydrate. In Table V wavenumbers of the thiocyanate vibrations are collected for the hydrate along with those of the α and β isomers. It is remarkable that two ν (CN) and two ν (CS) absorptions are found for the hydrate. For a square-planar conformation of the two thiocyanates and two ligands one would expect only one for a trans orientation and one also for a cis orientation.² On the basis of the position

Table V. Infrared Spectral Data of α - and β -[Cu(NCS)₂(dmtp)₂]₂ and Cu(NCS)₂(dmtp)₂·H₂O: Thiocyanate and Metal-Ligand Vibrations^a

assignts	comps		
	α	β	hydrate
ν (CN)	2109 s 2079 s	2098 s 2070 s	2105 m 2086 vs
ν (CS)	832 vw 779 m	830 vw 740 vw	829 vw 763 m
δ (NCS)	474 m	469 m	478 m
2 δ (NCS)	949 m	928 m	952 w
ν (Cu-OH ₂)			364 m
ν (Cu-N ₃ (lig)) _{asym}	282 s, sh	291 m, sh	300 w, sh
ν (Cu-N ₃ (lig)) _{sym}	243 m	267 m	283 s
ν (Cu-NCS(eq,T))	304 s, sh	308 s	307 s
ν (Cu-NCS(eq,B))	293 s		
ν (Cu-NCS(ax,B))			
ν (Cu-SCN(eq,B))			
ν (Cu-SCN(ax,B))	206 s		
ν (Cu-SCN)			245 s

^a Abbreviations: T = terminal, B = bridging, eq = equatorial, ax = axial.

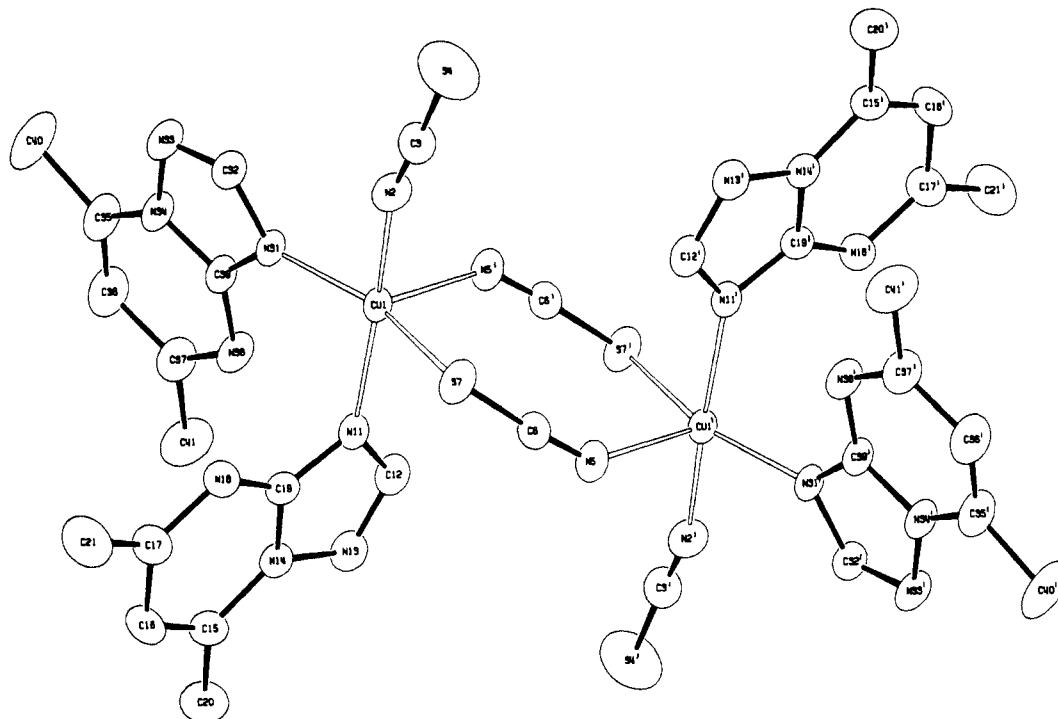
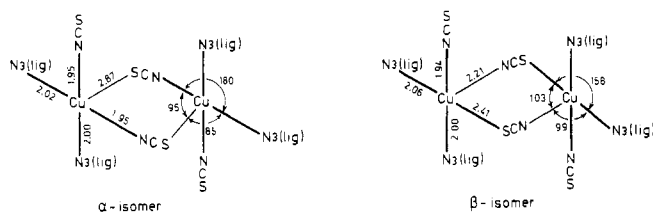
of both ν (CS) absorptions, 829 and 763 cm⁻¹, we suppose that one of the two NCS groups is bonded via S to copper.¹⁷ This

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Table VI. Ligand Field, ESR, and Magnetic Susceptibility Data of Cu(II) Thiocyanates Containing dmtp

compd	proposed (*) or proven chromophore	color	LF ² max, cm ⁻¹ × 10 ³	g at $\Delta m = 2$	g values	$\mu(80\text{ K}),$ μ_B	$\Theta(10-80\text{ K}),$ K
α	Cu(N ₄)S	dark green	15.9 (14.9) ^a	4.09	2.05 (g_{\perp}) 2.27 (g_{\parallel})	1.95 (3)	0.0 ± 0.5
β	Cu(N ₃ S)N	dark brown	14.4 (13.4) ^a	4.15	2.06 (g_{max}) 2.25 (sh)	1.78 (3)	1.0 ± 1.0
hydrate	*Cu(N ₃ S)O	green	13.7		2.12 (g_{max})		
Cu ²⁺ in Cd(NCS) ₂ (dmtp) ₂ (H ₂ O) ₂	CuN ₄ O ₂ (cis)	yellow	12.6		2.07 (g_{\perp}) 2.39 (g_{\parallel})		

 $(A_{\parallel} = 0.0105\text{ T})$ ^a Shoulder in parentheses.Figure 2. ORTEP drawing of β -[Cu(NCS)₂(dmtp)₂]₂, showing the atomic labeling system used in the structure determination. Primed atoms are generated by inversion.Figure 3. Basic molecular structures of α - and β -[Cu(NCS)₂(dmtp)₂]₂, showing relevant distances and angles. The heavy bonds around the copper atoms show the (distorted) square base of the square-pyramidal coordination.

may be correlated with the fact that the hydrate rearranges easily to β -[Cu(NCS)₂(dmtp)₂]₂ with the short equatorial Cu–SCN bond. Additional arguments come from the far-infrared part of the spectrum: the hydrate spectrum bears some similarity to the spectrum of the β isomer, apart from a prominent absorption at 366 cm⁻¹, attributed to a Cu–O stretching vibration. On the basis of the known structures of the α and β isomers a tentative assignment of the far-infrared spectra of the three compounds has been added to Table V. The ligand field spectra for all three compounds (Table VI, vide infra) agree with square-pyramidal geometry.¹⁸

Magnetic Susceptibility and ESR Measurements. The dimeric structure for the β isomer raised the question whether or not the magnetic exchange is different from the α -isomer. Table VI lists the ESR data and the magnetic susceptibilities, together with the ligand field maxima. For comparison the data of 5% Cu²⁺ doped in *cis*-Cd(NCS)₂(dmtp)₂(H₂O)₂ have been included. Both the α and the β isomer show the presence of weak $\Delta m = 2$ lines near $g = 4.2$ that are typical for Cu(II) dimers.¹⁹ The hydrate clearly is not a dimer. However, no splitting of g_{\parallel} into four lines is observed. This is quite common for magnetically undiluted Cu(II) species.¹⁸ The ESR spectra of the two dimers do not yield enough information to determine the magnitude of the zero-field splitting.¹⁹ Apparently, here the dimers are too close together in the lattice, resulting in exchange narrowing. The magnitude of the magnetic exchange can be determined by low-temperature magnetic susceptibility. Surprisingly, the powder magnetic susceptibility of the α isomer showed no evidence for significant magnetic interaction. The β isomer seems to be weakly ferromagnetic, although at low temperature the θ value drops to zero. The origin for such a weak magnetic exchange can be understood after consideration of the two X-ray structure. The magnetic orbitals, i.e. those holding the unpaired electron, in both isomers are not

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coplanar and parallel. This is now known to result in weak exchange between the metals.^{20,21}

Concluding Remarks

The results of the present study have once again illustrated that thiocyanate anions are, especially with Cu²⁺, versatile ambidentate ligands. The two distortion isomers (α and β) of [Cu(NCS)₂(dmtmp)₂]₂ are the first examples, to the best of our knowledge, of this isomerism in dinuclear Cu(II) compounds. The magnetic exchange coupling between the Cu²⁺ ions in the dimers is very small in each isomer and could be deduced only spectroscopically from the ESR data. Even ESR spectra are sometimes nonconclusive for the presence of dimers,

as recently shown by Hatfield,²² therefore, we cannot completely exclude that the hydrate Cu(NCS)₂(dmtmp)₂H₂O is oligomeric, despite the fact that far-infrared spectra point toward coordinated water in a mononuclear species.

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Registry No. Cu(NCS)₂(dmtmp)₂H₂O, 90991-02-9; α -[Cu(NCS)₂(dmtmp)₂]₂, 91050-44-1; β -[Cu(NCS)₂(dmtmp)₂]₂, 90991-03-0.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Formation, Crystal Structure, and EPR Spectroscopic Properties of a Heteronuclear (Pt₂, Cu) Mixed-Nucleobase (1-Methylcytosine, 1-Methyluracil) Complex: Bis[(μ -1-methyluracilato-*N*³,*O*⁴)(μ -1-methylcytosine-*N*³,*O*²)-*cis*-diammineplatinum(II)]-copper(II) Tetranitrate-6-Water

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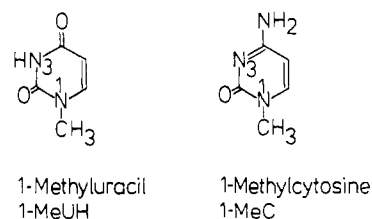
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The mixed-nucleobase complex *cis*-diammine(1-methylcytosine-*N*³)(1-methyluracilato-*N*³)platinum(II) nitrate, [Pt(NH₃)₂(C₅H₇N₃O)(C₅H₅N₂O₂)]NO₃·2H₂O (**1**), has been prepared and characterized by using ¹H NMR, IR, and Raman spectroscopy. NMR spectra show that in acidic medium the 1-MeU ligand becomes protonated (p*K*_a \approx 0.9) and in a slow secondary reaction releases neutral 1-methyluracil. The p*K*_a of the NH₂ (*N*⁴) group of *N*³-platinated 1-methylcytosine in **1** has been estimated to be ≥ 14 . In the presence of Cu(II), **1** forms a trinuclear complex **2**, bis[(μ -1-methyluracilato-*N*³,*O*⁴)(μ -1-methylcytosine-*N*³,*O*²)-*cis*-diammineplatinum(II)]copper(II) tetranitrate-6-water, [Pt(NH₃)₂(C₅H₅N₂O₂)(C₅H₇N₃O)Cu(C₅H₇N₃O)(C₅H₅N₂O₂)(NH₃)₂Pt](NO₃)₄·6H₂O. The crystal structure of this heteronuclear complex has been determined. The compound crystallizes in space group *P* $\bar{1}$, with cell dimensions *a* = 11.522 (6) Å, *b* = 10.924 (4) Å, *c* = 10.736 (2) Å, α = 91.51 (3)°, β = 109.08 (3)°, γ = 114.43 (3)°, and *Z* = 1. The structure was refined to *R* = 0.051 and *R*_w = 0.054 on the basis of 2603 reflections. Both Pt atoms are bound to *N*³ of 1-methyluracil and *N*³ of 1-methylcytosine, respectively, while Cu binds to *O*⁴ of uracil and *O*² of cytosine in pairs. All three metals have square-planar coordination spheres, with Cu sitting in the inversion center of the Pt₂Cu unit. The Pt-Cu distances within the cation are 2.681 (1) Å. Cu-O distances to 1-methyluracil (1.931 (12) Å) and 1-methylcytosine (1.988 (9) Å) do not differ greatly. EPR spectra, at X- and Q-band frequencies, are consistent with a tetragonally elongated ligand field about the Cu²⁺ ion in **2** and also in the related complexes *cis*-[(NH₃)₂Pt(1-MeU)₂Cu(1-MeU)₂Pt(NH₃)₂]²⁺. The spectra are compared with those of the dinuclear complex *cis*-[(NH₃)₂Pt(1-MeU)₂Cu(H₂O)₂]²⁺ for which a significant dipolar coupling between the Cu²⁺ ions in a centrosymmetrically related pair of cations in the unit cell is observed.

Introduction

The ligating properties of the individual pyrimidine nucleobases 1-methylcytosine and 1-methyluracil and their respective analogues toward metal ions have been extensively studied over the past years,² with the purpose of better understanding the more complex reactions of metal ions with nucleic acids (Chart I). As a result, it has become evident that there is a versatility in the binding patterns of these two nucleobases, depending on pH and the metals present. It has

Chart I



also been demonstrated that different metals may be bound simultaneously to the deprotonated 1-methyluracil ligand, 1-MeU, or its 1-methylthymine analogue, e.g. *cis*-(NH₃)₂Pt^{II}, Ag(I), Mn(II), Cu(II), and Na(I)³ or CH₃Hg^{II} and Na(I),⁴

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