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Registry No. $C_{12}H_9TeI_3$, 55776-30-2.

Supplementary Material Available: Table IV, the calculated (idealized) positions and assigned isotropic thermal parameters of the hydrogen atoms, Table V, the root-mean-square amplitudes of vibration, and Table VI, the observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

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Molecular Structure of Aquodipyridinecopper(II) Dithiodipropionate, $Cu(O_2CCH_2CH_2S-)_2 \cdot 2C_5H_5N \cdot H_2O$

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The crystal and molecular structure of the title complex has been determined from single-crystal three-dimensional x-ray data collected by counter methods. Cu(DTDP)·2py·H_2O (DTDP = dithiodipropionate) crystallizes as light blue rectangular plates in space group $Pna2_1$ (C_{2v}^9, No. 33) with $Z = 4$; $a = 22.268$ (15), $b = 14.855$ (12), $c = 5.670$ (4) Å; $d_{calcd} = 1.583$, $d_{obsd} = 1.57$ (1) g/cm^3. Least-squares refinement of 1077 reflections having $F \geq 2\sigma$ gave a conventional R factor of 0.071. The structure contains no discrete molecules; it consists of crystallographically equivalent Cu(II) ions linked by the DTDP ligands to form infinite chains with alternating left- and right-handed disulfide chirality for adjacent DTDP ligands. A trans puckered arrangement of two pyridine nitrogen atoms and two carboxylate oxygen atoms forms the base of the approximately square-pyramidal CuN_2O_3 ligand set. Cu–N bond lengths (2.02 (1), 2.06 (1) Å) and Cu–O(carboxylate) bond lengths (1.95 (1), 1.95 (1) Å) are appropriate for equatorial ligation. The Cu(II) ion is displaced 0.21 Å from this CuN_2O_2 plane toward an apically bonded water molecule (Cu–O(H_2O) = 2.23 (1) Å). Bonding interactions between the Cu(II) ions and disulfide groups are not implied from the structural data. The title complex was crystallized from pyridine–water mixtures of a dark green precursor with the empirical formula Cu^{II}DTDP·$^1/_2H_2O$. Electronic spectral and magnetic ($\mu = 1.40$ (5) μ_B) studies of this latter complex indicated the presence of ($\sim CO_2)_4Cu_2$ dimeric units; however, further studies are required to establish whether the crystal contains discrete molecular dimers or is polymeric. Pseudoisotropic ESR spectra ($g = 2.08$) of the title complex are presented and discussed.

Introduction

The coordination geometry and molecular structure of copper(II)–L-cystinate complexes (cystinate = ($O_2CCH(NH_2)CH_2S-)_2$) remain a poorly charted area of copper(II)–amino acid chemistry. Both the variety and the poor solubility of the aqueous copper(II)-L-cystinate solution species have restricted the scope of solution studies. However, a combination of detailed solution equilibria studies and careful structural analyses led Hawkins and Perrin to conclude that a dimeric species, di-μ-cystinato-dicopper(II), was a major component of aqueous copper(II)–L-cystinate systems.[2] Studies of molecular models established that both amino acid fragments of L-cystine could not bind to the same Cu(II) ion, implying that the solution dimer was ligand-bridged. A subsequent crystallographic study of a bis-μ-(D-penicillamine disulfide)-dicopper(II) complex (the ligand is tetramethylcystine) supported this inference.[3] However, it is not yet known whether the difficultly soluble copper(II)–L-cystinate complexes are ligand-bridged dimers or ligand-bridged polymers. Moreover, details of the coordination structure such as cis/trans attachment of the amino acid fragments, the possible binding by disulfide, etc., remain unknown. These issues were addressed in part in a study of microcrystalline and needle modifications of Cu^{II}-L-cys·H_2O (cys = cystinate) which will be presented elsewhere.[4] Unfortunately, neither cystine complex could be obtained in a form suitable for a single-crystal x-ray diffraction study. Because of its structural relationship to cystine, complexes of ($^-O_2CCH_2CH_2S-)_2$ (dithiodipropionate or DTDP) may bear indirectly on the above structural questions. We report here the synthesis and molecular structure of Cu^{II}DTDP·2py·H_2O. The preparation of a pyridine-free precursor of composition Cu^{II}DTDP·$^1/_2H_2O$ is also reported.

Experimental Section

Preparation of $Cu(O_2CCH_2CH_2S-)_2 \cdot {}^1/_2H_2O$ (I). A solution containing 4.20 g of ($HO_2CCH_2CH_2S-)_2$ (0.02 mol) and 0.34 g of $NaHCO_3$ (0.04 mol) in 250 ml of distilled H_2O was heated to 60 °C to expel CO_2 and filtered through a 0.22-μm pore size membrane. Addition of a similarly filtered solution of 3.40 g (0.02 mol) of $CuCl_2 \cdot 2H_2O$ in 100 ml of distilled water to the ligand solution resulted in the precipitation of a dark green microcrystalline product. The product was collected by filtration, thoroughly washed with H_2O, acetone, and ether, and air-dried. The yield was quantitative. Anal. Calcd for $CuC_6H_8O_4S_2 \cdot {}^1/_2H_2O$: C, 25.67; H, 3.23. Found: C, 25.8; H, 3.1.

Preparation of $Cu(O_2CCH_2CH_2S-)_2 \cdot 2py \cdot H_2O$ (II). A deep blue stock solution was obtained by adding 6.0 g of I to a mixture of 100 ml of distilled water and 30 ml of pyridine (dissolution of I was not immediate) and diluting the resulting solution to 200 ml with additional

Table I. Crystal Data for $Cu(O_2CCH_2CH_2S-)_2 \cdot 2C_5H_5N \cdot H_2O$

Mol wt 448.02
Space group $Pna2_1$ (C_{2v}^9, No. 33)
$Z = 4$
$a = 22.268$ (15) Å
$b = 14.855$ (12) Å
$c = 5.670$ (4) Å
$V = 1879.4$ Å^3
$d_{\mathrm{calcd}} = 1.583$ g/cm^3
$d_{\mathrm{obsd}} = 1.57$ (1) g/cm^3
λ 0.710 69 Å
$T = 25$ (1) °C
$\mu = 14.47$ cm^{-1} for Mo Kα

H_2O. A mixture of one part stock solution and eight parts H_2O was filtered as above and placed in a partially covered beaker. Partial evaporation of pyridine (and H_2O) in air at 25 °C resulted in the formation of pale blue rectangular plates. Substantially greater dilution (i.e., lower pyridine concentration) resulted in the formation of crystalline I. The blue crystals were collected by filtration, washed with water and acetone (poor solubility), air-dried, and stored in a sealed container. Yields were essentially quantitative. Exposure of II to air at 25 °C resulted in the slow loss of pyridine and reversion to I. This process was accelerated by heating in a melting point apparatus; a sharp change in color from light blue to green occurred at ~103 °C. Anal. Calcd for $CuC_{16}H_{18}O_4N_2S_2 \cdot H_2O$: C, 42.90; H, 4.50. Found: C, 42.9; H, 4.4.

Magnetic Susceptibility. The magnetic susceptibilities of I and II were measured at 20 °C using a Gouy apparatus calibrated with $Ni(en)_3 \cdot S_2O_3$. Finely powdered II rapidly lost pyridine. Because the possible error due to nonrandom crystal orientation appeared less formidable than that expected from sample decomposition, complex II was studied in the form it was obtained. Contamination of I and II was minimized by membrane filtration of reagent solutions (vide supra). The effective absence of ferromagnetic impurities was indicated by the invariance of the observed susceptibilities to the field strength of the electromagnet (~2000–~10 000 G). Magnetic susceptibilities were corrected for diamagnetism; corrections of -136×10^{-6} and -244×10^{-6} cgsu were applied to the molar susceptibilities obtained for I and II, respectively. Diamagnetic susceptibilities are known for H_2O,[5] pyridine,[5] and Cu(II);[6] that for DTDP[5] was estimated by doubling that reported for butyric acid and adding -30×10^{-6} cgsu for the two sulfur atoms.

ESR Spectra. X-Band ESR spectra were obtained at 25 °C on a Varian Model E-12 spectrometer and calibrated using a DPPH crystal ($g = 2.0036$) and a Hewlett–Packard Model 5245L frequency counter. Precautions to ensure the random orientation of II were not taken (see previous paragraph).

Electronic Spectra. Reflectance spectra were measured with a Cary Model 14 spectrophotometer. A block of $MgCO_3$ was used as the reference.

Collection and Reduction of Diffraction Data. A single crystal of II having dimensions of 0.41 × 0.14 × 0.03 mm was mounted in a sealed capillary (0.3-mm diameter) along its longest dimension. Unit cell constants (Table I), determined at room temperature using a $P2_1$ Syntex diffractometer and Mo Kα radiation, were obtained from a least-squares fit of 10 moderately intense reflections. A quick scan of the various classes of reflections revealed the following systematic absences: $0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$. These absences are consistent with two space groups: $Pna2_1$ (C_{2v}^9, No. 33) and $Pnam$ (D_{2h}^{16}, No. 62). The structure was refined successfully in the noncentrosymmetric space group $Pna2_1$. The density was measured by flotation in a mixture of CCl_4 and diethyl ether. The observed density of 1.57 (1) g/cm^3 was in good agreement with the calculated value of 1.583 g/cm^3 based on four molecules of II per unit cell.

Intensity data were collected at 25 (1) °C using a θ–2θ scan to a maximum of $2\theta = 60°$. Each scan covered a range of 0.7° below $K\alpha_1$ and 0.9° above $K\alpha_2$ for the calculated peak position. All data were collected using a scan rate of 2.55° min^{-1} with stationary-background counts taken before and after each scan. The total time for background counts equaled the scan time and was equally distributed before and after the peak. Two standard reflections were recorded at intervals of 48 reflections throughout the data collection. They showed a random variation of 1.4% and no significant trends. A total of 1077 unique reflections (from a total of 3191) with $F(\sigma) > 2\sigma$ were used in the structure solution and refinement. Intensities were calculated from $I = (P - LB - RB)S$, where P is the peak count, LB the left-background count, RB the right-background count, and S the scan rate. These intensities were placed on a common scale by correcting for decay on the basis of the two standard reflections and for Lorentz and polarization effects. Absorption corrections were not applied. Absorption factors ranged from 1.04 to 1.23 using a linear absorption coefficient of 14.47 cm^{-1} for Mo Kα radiation. The maximum effect of absorption on values of F is, therefore, approximately ±2%. An estimate of the overall scale factor was obtained using Wilson's method and was subsequently refined.

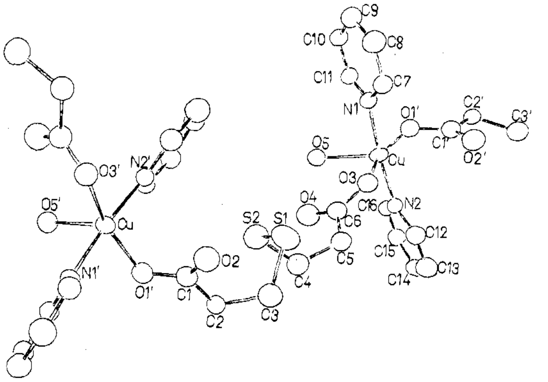


Figure 1. Structure of II, showing the atom numbering scheme.

Structure Determination. The structure was solved by the heavy-atom method and refined using full-matrix least-squares techniques.[7] Approximate coordinates for the unique copper and two sulfur atoms were obtained from a normal sharpened Patterson map. Space group $Pna2_1$ (noncentrosymmetric) differs from $Pnam$ (centrosymmetric) by the presence of a mirror plane at $z = {}^1/_4$. Both the Cu and S atom coordinates obtained from the Patterson analysis (Table II) are consistent with the presence of this symmetry element; therefore, their coordinates could not be used to distinguish between the possible space groups. The coordinates of the remaining nonhydrogen atoms were located via a series of structure factor, difference Fourier calculations. As the analysis progressed, it became apparent that the mirror plane at $z = {}^1/_4$ could not be maintained. This can be seen, for example by examining the structure in the vicinity of the disulfide group (Figure 1). If S(1) and S(2) are mirror images, then C(3) must lie on the mirror plane; the angle S(2)–S(1)–C(3) must then be less than 90°, which is unacceptable. Consequently, analysis in space group $Pnam$ was abandoned. With all nonhydrogen scattering matter present, the initial agreement factor $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.25.

Isotropic refinement was initiated using atomic scattering factors from Cromer and Waber[8] for Cu, S, O, N, and C. All atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion correction were applied to Cu and S.[9] Initial refinement was based on F^2 and unit weights were employed. Several cycles of refinement resulted in the isotropic convergence of R_F at 0.115.

Further refinement was based on F and a weighting scheme was chosen by an analysis of variance to make $\Delta F/\sigma$ independent of F_o. This procedure led to assignments for $\sigma(F_o)$: $\sigma(F_o) = 3.258 - 0.104|F_o|$, $0 < |F_o| < 14.6$; $\sigma(F_o) = 1.048 + 0.048|F_o|$, $|F_o| > 14.6$.

Except for those of the H_2O molecule, hydrogen coordinates were calculated. These hydrogen atoms were added as a fixed atom contribution to the overall structure factor calculation. The temperature factor used for the H atoms was that obtained from the Wilson plot. Several cycles of refinement using anisotropic temperature factors for the Cu and S atoms led to convergence with R_F at 0.071 and the function $R_{wF} = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ at 0.093. All positional and thermal parameter changes were within their estimated standard deviation for the last cycle of refinement. A final difference Fourier showed a general background of approximately 0.3 e/Å^3 and no peaks larger than 1.1 e/Å^3. All peaks above background were residuals of known atoms.

Final atomic parameters are given in Table II. A list of observed and calculated structure factors is available.[10]

Results and Discussion

Description of the Structure. Views of the structure and its packing are shown in Figures 1 and 2, respectively. There are no discrete complexes in the structure. It consists of crystallographically equivalent Cu(II) ions linked by DTDP ligands to form infinite chains along a. Adjacent DTDP ligands in a given chain show alternating left- and right-handed disulfide

Table II. Fractional Atomic Coordinates and Thermal Parameters[a,b] for Cu(DTDP)·2py·H_2O

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	1544 (1)	1240 (1)	2500	103 (3)	219 (6)	2134 (49)	2 (6)	37 (24)	−134 (38)
S(1)	3865 (2)	1418 (4)	5473 (13)	165 (10)	459 (27)	3838 (218)	−73 (14)	201 (44)	−163 (77)
S(2)	4226 (2)	1475 (3)	2247 (16)	144 (8)	491 (26)	4225 (267)	−43 (12)	72 (52)	116 (24)

	x	y	z	B, Å^2		x	y	z	B, Å^2
O(1)	2238 (4)	437 (7)	2397 (34)	2.8 (2)	H1(C2)	3330	120	2238	2.5
O(2)	2395 (6)	781 (9)	6064 (27)	3.7 (3)	H2(C2)	3094	−747	4043	2.5
O(3)	5925 (5)	2965 (8)	3768 (27)	3.0 (2)	H1(C3)	3982	−203	5637	2.5
O(4)	5745 (6)	2229 (10)	500 (31)	4.5 (3)	H2(C3)	3412	150	7465	2.5
O(5)	1365 (5)	1259 (9)	−1348 (24)	3.0 (2)	H1(C4)	5168	774	1214	2.5
N(1)	1010 (6)	152 (8)	2958 (26)	2.2 (3)	H2(C4)	4922	388	3834	2.5
N(2)	2146 (5)	2286 (8)	2228 (29)	2.2 (3)	H1(C5)	5180	1918	5498	2.5
C(1)	2537 (8)	442 (12)	4260 (37)	2.7 (4)	H2(C5)	5740	1180	4881	2.5
C(2)	3149 (7)	−31 (11)	3973 (34)	2.3 (3)	H(C7)	636	492	6226	2.5
C(3)	3605 (8)	254 (13)	5783 (41)	3.5 (4)	H(C8)	15	−887	6534	2.5
C(4)	4967 (7)	1009 (11)	2758 (48)	3.6 (4)	H(C9)	101	−2075	3432	2.5
C(5)	5461 (8)	1592 (13)	4061 (37)	2.9 (4)	H(C10)	747	−1747	2	2.5
C(6)	5711 (7)	2310 (10)	2598 (50)	2.9 (3)	H(C11)	1360	−387	−117	2.5
C(7)	657 (8)	−8 (12)	4837 (35)	2.8 (4)	H(C12)	1843	2990	5197	2.5
C(8)	315 (9)	−788 (14)	5074 (43)	3.8 (4)	H(C13)	2598	4210	4770	2.5
C(9)	356 (9)	−1448 (12)	3311 (35)	3.2 (4)	H(C14)	3295	4174	1522	2.5
C(10)	720 (8)	−1260 (12)	1443 (34)	2.5 (3)	H(C15)	3332	2826	−1122	2.5
C(11)	1050 (8)	−484 (11)	1349 (35)	2.4 (3)	H(C16)	2528	1683	−649	2.5
C(12)	2166 (8)	2970 (13)	3738 (40)	3.1 (4)					
C(13)	2588 (9)	3650 (14)	3537 (38)	3.8 (4)					
C(14)	2977 (8)	3625 (12)	1772 (33)	2.9 (4)					
C(15)	2991 (8)	2892 (12)	226 (39)	3.0 (4)					
C(16)	2545 (7)	2252 (11)	521 (38)	2.4 (3)					

[a] Atomic coordinates are ×10^4. [b] Anisotropic thermal parameters are ×10^5; the form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

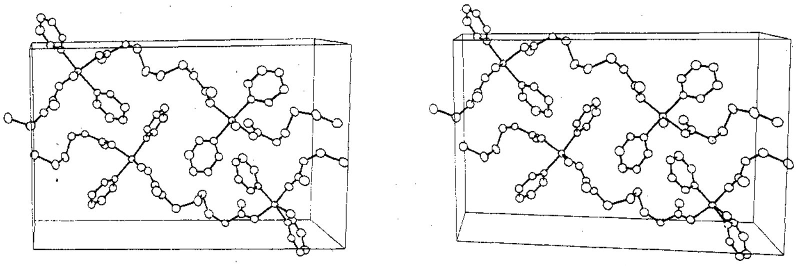
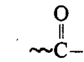


Figure 2. Stereoscopic view of the unit cell contents viewed along a.

chirality as required by the a glide plane which is perpendicular to b and approximately parallel to the polymer axis.

The trans puckered arrangement of pyridine nitrogen atoms N(1) and N(2) and carboxylate oxygens O(3) and O(1′) forms the base of an approximately square-pyramidal CuN_2O_3 ligand set. Equatorial bonding within the pseudoplanar Cu, N(1), N(2), O(3), O(1′) unit is established by the respective Cu–N(1) and Cu–N(2) bond lengths of 2.02 (1) and 2.06 (1) Å and by the equivalent Cu–O(1′) and Cu–O(3) bond lengths of 1.95 (1) Å; these values are not unusual for Cu(II) complexes.[11] The Cu(II) ion is displaced about 0.21 Å from the best plane of these basal ligand atoms toward the water oxygen atom O(5) which occupies the fifth coordination site. The observed Cu–O(5) bond distance of 2.23 (1) Å establishes the H_2O ligation as apical. The overall coordination environment is quite similar to that observed for bis[(D-penicillamine disulfide)copper(II)]-9-water,[3] another Cu(II) complex with a cystine-related ligand. An important difference between these structures is the apparent absence of a Cu^{II}–S bonding interaction in complex II where the shortest Cu···S distance is 5.443 Å. Pseudotetragonal CuN_2O_3S ligation would seem to be structurally feasible for II, and consistent with the terdentate nature of DTDP indicated by studies[2] of the aqueous Cu^{II}–DTDP system; however, this is not observed in the present structure.

Structural parameters of the pyridine and DTDP ligands are not unusual, and will not be considered in detail. Both carboxylate groups of DTDP are monodentate and exhibit C–O bond distances appropriate for



$$\sim\overset{\overset{\displaystyle O}{\|}}{C}-O$$

units. Bond distances, bond angles, and torsional angles for molecules containing aliphatic C–S–S fragments have been summarized by Jones et al.[12] The S–S bond distance of 2.01 (1) Å in II lies near the short end of the range [2.00–2.084 Å] reported for such linkages. Short S–S disulfide linkages are thought[12] to result from the minimal sulfur lone-pair repulsions associated with a torsional angle of ~90°. The observed torsional angle [81.6 (9)°] in II is consistent with this interpretation.

Magnetic Studies. The relatively large Cu(II)···Cu(II) separation (5.700 (4) Å between chains) and the absence of superexchange pathways ensures that II is a magnetically dilute complex. This is also indicated by the normal magnetic moment of 1.90 (5) μ_B. Structural features of II which are relevant to its ESR spectra include (a) magnetic dilution, (b) chemically different principal axes, i.e., the N(1)–N(2), O(3)–O(1′), and Cu–O(5) directions, (c) the different orientations of these principal axes within the unit cell (see Figure 2), and (d) the absence of symmetry constraints on the Cu(II) ions. Rhombic (three-component) ESR spectra typically are observed for powdered samples of *trans*-Cu(amino acid)$_2$·(0–2)H_2O complexes.[13] In contrast, the spectra of II consist

Table III. Bond Distances (Å) and Angles (deg) in $\mathrm{Cu(DTDP)\cdot 2py\cdot H_2O}$

Distances

Cu–O(1)	1.95 (1)	O(3)–C(6)	1.27 (2)
Cu–O(3)	1.95 (1)	O(4)–C(6)	1.20 (3)
Cu–O(5)	2.23 (1)	N(1)–C(7)	1.35 (2)
Cu–N(1)	2.02 (1)	C(7)–C(8)	1.39 (3)
Cu–N(2)	2.06 (1)	C(8)–C(9)	1.41 (3)
Cu· · ·Cu[a]	5.700 (4)	C(9)–C(10)	1.37 (3)
O(1)–C(1)	1.25 (3)	C(10)–C(11)	1.37 (2)
O(2)–C(1)	1.19 (2)	C(11)–N(1)	1.32 (2)
C(1)–C(2)	1.54 (2)	N(2)–C(12)	1.33 (2)
C(2)–C(3)	1.51 (3)	C(12)–C(13)	1.39 (3)
C(3)–S(1)	1.83 (2)	C(13)–C(14)	1.33 (3)
S(1)–S(2)	2.01 (1)	C(14)–C(15)	1.40 (3)
S(2)–C(4)	1.81 (2)	C(15)–C(16)	1.39 (2)
C(4)–C(5)	1.50 (3)	N(2)–C(16)	1.32 (2)
C(5)–C(6)	1.52 (3)		

Angles

O(1)–Cu–O(3)	159.8 (7)	C(10)–C(11)–N(1)	123 (2)
O(1)–Cu–O(4)	152.9 (6)	C(16)–N(2)–C(12)	119 (1)
O(1)–Cu–O(5)	96.9 (6)	N(2)–C(12)–C(13)	122 (2)
O(1)–Cu–N(1)	88.9 (5)	C(12)–C(13)–C(14)	119 (2)
O(1)–Cu–N(2)	86.7 (4)	C(13)–C(14)–C(15)	121 (2)
N(1)–Cu–N(2)	174.6 (6)	C(14)–C(15)–C(16)	116 (2)
N(1)–Cu–O(5)	91.9 (5)	C(15)–C(16)–N(2)	123 (2)
N(1)–Cu–O(3)	91.2 (5)	O(1)–C(1)–O(2)	126 (2)
N(2)–Cu–O(3)	91.8 (5)	O(1)–C(1)–C(2)	112 (2)
N(2)–Cu–O(5)	91.8 (6)	O(2)–C(1)–C(2)	121 (2)
Cu–N(1)–C(11)	116 (1)	C(1)–C(2)–C(3)	113 (2)
Cu–N(1)–C(7)	126 (1)	C(2)–C(3)–S(1)	114 (1)
Cu–N(2)–C(12)	123 (1)	C(3)–S(1)–S(2)	105 (1)
Cu–N(2)–C(16)	118 (1)	S(1)–S(2)–C(4)	102 (1)
Cu–O(1)–C(1)	113 (1)	S(2)–C(4)–C(5)	117 (1)
Cu–O(3)–C(6)	122 (1)	C(4)–C(5)–C(6)	115 (2)
C(11)–N(1)–C(7)	118 (1)	C(5)–C(6)–O(3)	115 (2)
N(1)–C(7)–C(8)	123 (2)	C(5)–C(6)–O(4)	120 (2)
C(7)–C(8)–C(9)	118 (2)	O(3)–C(6)–O(4)	125 (2)
C(8)–C(9)–C(10)	117 (2)	C(3)–S(1)–S(2)/ S(1)–S(2)–C(4)	81.6 (9)
C(9)–C(10)–C(11)	121 (2)		

[a] Interchain separation. The separation of Cu(II) ions bonded to the ends of a common DTDP ligand is 11.749 (4) Å.

Table IV. Deviations from Least-Squares Plane[a]

Atom	Dist from plane, Å	Atom	Dist from plane, Å
O(1)	0.140	N(2)	−0.135
O(3)	0.131	Cu	−0.205
N(1)	−0.136		

[a] Plane defined by Cu, O(1′), O(3), N(1), N(2).

of an essentially isotropic absorption centered at $g = 2.08$; a poorly resolved low-symmetry component is present at $g \simeq 2.1$. The relationship of pseudoisotropic spectra to structural feature (c) has been reviewed elsewhere.[14] Presumably, this effect accounts for the observed ESR spectra of the title complex.

The ESR spectra of complex I were severely broadened and difficult to observe. This result was not surprising in view of its reduced paramagnetism (1.40 (8) μ_B). Both the magnetic results and the optical absorption (reflectance) of I at ~370 nm are typical of copper(II) carboxylates which have the $\mathrm{Cu_2(OAc)_4}$ structure.[15] The spectra of complex I also include a band at ~670 nm which is assigned to the expected ligand field absorption, and a band at ~260 nm which is assigned to a mixture of $\mathrm{CO_2} \rightarrow \mathrm{Cu(II)}$ charge-transfer and localized disulfide absorptions.[16] Dimeric copper(II) carboxylates typically exhibit relatively intense ligand field absorption. Although the color of I was a suspiciously dark green, the extreme insolubility of the complex in common solvents prevented our obtaining an ϵ for the ligand field absorption.

Further studies are required to establish whether I crystallizes as discrete molecular dimers or as polymeric chains similar to those observed for copper(II) succinate.[15] Neither structural type was evident in solution studies of the aqueous $\mathrm{Cu^{II}}$–DTDP system.[2] However, the dimeric structure of the "parent" $\mathrm{Cu_2(OAc)_4\cdot 2H_2O}$ complex is not retained in strongly coordinating solvents such as $\mathrm{H_2O}$,[17] and solution studies could be misleading. The solution studies did indicate a ligand role for disulfide.[2] Assuming that complex I does adopt the $\mathrm{Cu_2(OAc)_4\cdot 2H_2O}$ or copper(II) succinate structure, each Cu(II) must have an equatorial $\mathrm{CuO_4}$ ligand set. If present, copper(II)–disulfide bonding would then be apical. Since equatorial copper(II)–thioether bonds (and presumably equatorial copper(II)–disulfide bonds) exhibit charge-transfer absorptions in the 350–450-nm region,[18-20] those for apical copper(II)–disulfide bonding should be relatively weak. The combined effects of the long apical bond distance and the localization of the Cu(II) d vacancy ($d_{x^2-y^2}$) in the plane of the equatorial ligands greatly reduce the intensity of charge-transfer absorptions for copper(II)–apical ligand chromophores.[20]

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Supplementary Material Available: Structure factor table (6 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures at –35 °C of Two Crystal Forms of Bis(2,6-dimethylpyridine)chromium, a Bis Heterocyclic Sandwich Complex

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The molecular structure of the heterocyclic sandwich complex bis(2,6-dimethylpyridine)chromium, $(C_7H_9N)_2Cr$, has been determined by single-crystal x-ray diffraction techniques using three-dimensional data gathered at –35 °C by counter methods. Deep red crystals obtained by vacuum thermal gradient sublimation exhibit two distinct morphologies: form A, bulky prisms of triclinic symmetry, space group $P\bar{1}$, $a = 7.307$ (1) Å, $b = 8.242$ (2) Å, $c = 6.316$ (2) Å, $\alpha = 112.50$ (3)°, $\beta = 104.01$ (2)°, $\gamma = 102.46$ (2)°, $Z = 1$; form B, thin plates of orthorhombic symmetry, space group *Pbcn*, $a = 9.421$ (1) Å, $b = 10.496$ (2) Å, $c = 12.725$ (2) Å, $Z = 4$. In both forms the molecule is a true sandwich complex consisting of a Cr atom symmetrically π bonded to two 2,6-dimethylpyridine ligands. In form A, Cr is located at a crystallographic inversion center, and accordingly the molecule has C_i symmetry, while in form B, Cr resides on a crystallographic twofold axis, so that here the molecule has C_2 symmetry. Except for a difference in conformation, the molecular geometry of $(C_7H_9N)_2Cr$ is the same in both crystal forms. Since the pyridine ligands of $(C_7H_9N)_2Cr$ are known to rotate freely in solution, these two crystal modifications (i.e., A and B) represent two different rotameric conformations of this fluxional molecule. Full-matrix least-squares refinement of the structure has converged with a conventional R index (on $|F|$) of 0.086 for form A using the 1064 reflections with $I_o > 2.0\sigma(I_o)$ and 0.045 for form B using 909 similarly selected observations.

Introduction

Numerous π-carbocyclic transition metal sandwich type complexes have been prepared since the discovery of the first such species, bis(π-cyclopentadienyl)iron or ferrocene, in 1952.[1] Among these are the bis(π-cyclopentadienyl)metal complexes of all 3d metals,[2] a host of bis(benzenoid)–transition metal compounds[2] (e.g., $(C_6H_6)_2Cr$[3]), and several mixed π-carbocyclic ligand–metal systems (e.g., $(C_5H_5)(C_4H_4)Co$[4] and $(C_5H_5)(C_3(C_6H_5)_3)Ni$[5]), as well as some lanthanide ($[Ce(C_8H_8)_2^-]$[6]) and actinide ($(C_8H_8)_2U$ and $(C_8H_8)_2Th$[7]) π complexes.

In contrast to these successes have been the efforts to synthesize analogous sandwich compounds with π-heterocyclic ligands. Although various "half-sandwich" complexes of the form $M(CO)_3L$, where M = Cr or Mn and L = neutral pyrrole or a pyrrolyl ligand,[8] thiophene,[9] substituted thiopyran,[10] or tri- or pentamethylpyridine,[11] have been prepared, the only reported examples of "full" heterocyclic sandwich compounds are those of the mixed-ligand species (π-cyclopentadienyl)(π-pyrrolyl)iron or azaferrocene, $(C_5H_5)(C_4H_4N)Fe$,[12] and its derivative $(C_5H_5)[C_4H(CH_3)_2(C(O)CH_3)N]Fe$.[13] We now wish to present the crystal and molecular structures of two conformational isomers of bis(2,6-dimethylpyridine)chromium, $(C_7H_9N)_2Cr$, a bis heterocyclic sandwich complex possessing identical (i.e., unmixed) ligands. A preliminary account of the synthesis and structure of this compound has appeared.[14]

Experimental Section

Because $(C_7H_9N)_2Cr$ decomposes in air (to a nonvolatile green substance (Cr_2O_3?)),[15] all sample manipulations were performed under N_2. Deep red crystals of the complex grown slowly by vacuum thermal gradient sublimation yielded crystals of two distinct morphologies: bulky prisms, henceforth form A, and thin plates, henceforth form B. In turn, a crystal of each form was attached to a glass fiber and then quickly transferred to a Syntex $P2_1$ diffractometer, where it was maintained in a stream of N_2 at ca. –35 °C. Preliminary diffraction experiments (with the diffractometer) suggested triclinic symmetry for form A, a suggestion ultimately confirmed by successful solution and refinement of the structure in space group $P\bar{1}$, but indicated the orthorhombic symmetry of space group *Pbcn* for form B. Crystal data for both forms of $(C_7H_9N)_2Cr$ are available in Table I.

As described below, in form A the molecules of $(C_7H_9N)_2Cr$ exhibit C_i symmetry. Comparison of the unit cell volumes of forms A and B (Table I) reveals that the unit cell of form B contains 4 molecules of the complex. Space group *Pbcn* could accommodate 4 molecules per unit cell at one of two different symmetry sites; at one the molecules would have C_i symmetry as in form A, but at the other they would have C_2 symmetry. If the C_2 sites were occupied in form B, then the molecular conformation of $(C_7H_9N)_2Cr$ in B *could* be different from that in A. (Clearly, however, the $(C_7H_9N)_2Cr$ molecules in B could reside at sites of C_2 symmetry and still retain the conformation found in A.) The NMR spectrum of $(C_7H_9N)_2Cr$ in toluene-d_8 shows free rotation of the pyridine rings to –65 °C.[14,15] Hence, isolation of different rotameric conformations of $(C_7H_9N)_2Cr$ would be consistent with this behavior.

A summary of data collection details is provided in Table I. Data reduction and assignment of standard deviations (with $p = 0.02$) to the measured intensities were carried out as described before.[16] Analysis of the check reflections of each data set (Table I) showed $(C_7H_9N)_2Cr$ to be stable during data collection (N_2 stream, –35 °C), so that corrections for decomposition were not needed. Following data collection, attempts to determine the diffractometer setting angles for the faces of the data crystal of form A failed, owing to rapid crystal decomposition in air; hence we were unable to apply an absorption correction to these data. However, a procedure (to cope with the air sensitivity of $(C_7H_9N)_2Cr$) was devised to achieve this for the data crystal of form B, so that these data were corrected for absorption.

Solution and Refinement of the Structures

Triclinic Form A. A difference Fourier map phased with Cr at the unit cell origin clearly revealed the positions of all nonhydrogen atoms. Full-matrix least-squares refinement, in centric space group $P\bar{1}$, first treating these atoms isotropically and then anisotropically, converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.097$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.118$ for the 1064 reflections with $I_o/\sigma(I_o) > 2.0$, where $\sigma(I_o)$ is the estimated standard deviation of a reflection of intensity I_o.[16] The function minimized in refinement[17] is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors were used for Cr,[18] N,[19] C,[19] and H,[20] and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[21] for anomalous scattering were applied to the Cr scattering function.

A difference Fourier map then indicated the hydrogen positions at heights of 0.6–1.1 and 0.3–0.7 e Å^{-3} for ring and methyl hydrogen atoms, respectively. For comparison, the carbon atoms of the initial difference map ranged in density from 6.5 to 6.9 e Å^{-3}. In the final cycles of least-squares refinement, the ring hydrogens were treated isotropically, but the methyl hydrogens which did not refine properly were constrained to idealized tetrahedral positions (C–H = 0.95 Å and N–C–C(methyl)–H torsion angles learned from form B). At convergence, the final error indices are $R = 0.086$ and $R_w = 0.106$, and a standard deviation of an observation of unit weight, $[\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2}$, is 5.30, where m (1064) is the number of observations $|F_o|$ and s (91) is the number of variables in least-squares refinement. When all 1131 reflections examined during data collection