of Ru(Et$_2$dtc)$_3$ and *cis*-Ru(Et$_2$dtc)$_2$(CO)$_2$. Additionally, the ^{1}H NMR spectrum of **2** in no way resembles the spectra of either of the above compounds. Clearly, further experiments are needed and are in progress.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, general temperature factor expressions, and weighted least-squares planes calculations (32 pages). Ordering information is given on any current masthead page.

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Studies of Chelation Therapy. Crystal and Molecular Structure of $Cu[H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2](ClO_4)_2$, Cu(2,3,2-tet)(ClO$_4$)$_2$

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The crystal and molecular structure of $Cu[H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2](ClO_4)_2$ has been determined from single-crystal, three-dimensional X-ray data collected by counter methods. Dark purple crystals precipitated from methanol/water in space group $P\bar{1}$ with $Z = 2$, $a = 12.996$ (9) Å, $b = 8.297$ (2) Å, $c = 8.549$ (4) Å, $\alpha = 113.11$ (3)°, $b = 83.93$ (5)°, $\gamma = 113.37(4)$°, $d_{\text{calcd}} = 1.807$ g/cm^3, and $d_{\text{obsd}} = 1.808$ (5) g/cm^3. Least-squares refinement of 2162 reflections having $F^2 > 3\sigma(F^2)$ gave a conventional R factor of 0.044. The structure consists of Cu^{II}(2,3,2-tet)(ClO$_4$)$_2$ monomers with characteristic N$_4$O$_2$ ligand donor sets. Equatorial ligation is provided by the quadradentate tetraamine and apical ligation by oxygen atoms from monodentate perchlorate groups, which, on the basis of bond distances, exhibit effective C_{3v} symmetry. The 2,3,2 tetraamine binds to Cu(II) in a relatively strain-free configuration as indicated by the stable gauche, chair, and gauche conformations of the linked five-, six-, and five-membered chelate rings. In contrast to related linear tetraamine derivatives of copper which have been characterized crystallographically, trans N–Cu–N angles in the title complex [176.4 (3), 178.5 (4)°] are close to 180° and the CuN$_4$ chromophore is approximately planar [±0.03 Å]. These structural features suggest that the N$_4$ ligand donor sets nearly match the symmetry properties of the Cu(II) orbitals and are consistent with the relatively high heat of formation and large stability constant of the title complex. The structure of the homologous Cu(3,3,3-tet)(ClO$_4$)$_2$ complex is described briefly.

Introduction

Wilson's disease results from an inherited metabolic disorder which leads to an accumulation of excess deposits of copper in the body. In most patients, this disease can be managed successfully by oral chelation therapy with D-penicillamine.[2] Unfortunately, D-penicillamine therapy is associated with a variety of toxic reactions and hypersensitivity. An alternate chelation therapy utilizing triethylenetetramine–bis(hydrogen chloride) has been used to maintain Wilson's patients who develop an absolute intolerance to D-penicillamine (approximately 10%).[3] However, triethylenetetramine is less effective than D-penicillamine in promoting urinary excretion of copper.

To help develop a more effective chelation therapy, we have compared the copper excretion of rats induced by D-penicillamine, triethylenetetramine–bis(hydrogen chloride), and other tetraamine ligands which exhibit large affinities for Cu(II).[4] The 2,3,2 tetraamine[5] $H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ exhibits a ~6000-fold larger formation constant[6] for Cu(II) than the homologous triethylenetetramine (2,2,2-tet). Moreover, 2,3,2-tet causes a greater and more sustained copper excretion than either 2,2,2-tet or D-penicillamine.[4]

To facilitate future pharmacological studies and help illuminate the factors responsible for its large formation constant, we have chosen to characterize the Cu(2,3,2-tet)$^{2+}$ complex in detail. We report here the crystal structure of Cu(2,3,2-tet)(ClO$_4$)$_2$ along with a comparison of its structural features with those reported for other Cu(II)–polyamine species. Preliminary structural features of the Cu(3,3,3-tet)(ClO$_4$)$_2$ complex are also described and used to help explain the large difference in formation constants between the Cu(2,3,2-tet)$^{2+}$ and Cu(3,3,3-tet)$^{2+}$ complexes.

Experimental Section

1. Preparation of Cu(2,3,2-tet)(ClO$_4$)$_2$. The 2,3,2 tetraamine was prepared according to a published procedure[7] from the reaction of 1,3-dibromopropane with excess ethylenediamine. The product was recovered by distillation (85–92 °C, 0.1 mm). An assay using HCl revealed that the dihydrate 2,3,2-tet·2H$_2$O was obtained.

After 2 days, dark purple prisms of the title complex crystallized from a chilled (~−10 °C) mixture of 80 mL of CH$_3$OH, 20 mL of H$_2$O, 0.75 g of Cu(ClO$_4$)$_2$·6H$_2$O (2.0 mmol), and 0.39 g of 2,3,2-tet·2H$_2$O (2.0 mmol). The product was collected by filtration, washed with 5 mL of 95/5 (v/v) CH$_3$OH/H$_2$O, and dried in air. Anal. Calcd for $CuC_7H_{20}N_4Cl_2O_8$: Cu, 15.03; N, 13.25; Cl, 16.77; C, 19.89; H, 4.77. Found: Cu, 15.03; N, 13.16; Cl, 16.69; C, 19.77; H, 4.74.

2. Collection of Diffraction Data. Pertinent details regarding crystal data, intensity data collection, and refinement are collected in Table I. Preliminary Weissenberg photographs were devoid of systematic absences, limiting the possible space groups to $P1$ or $P\bar{1}$. Successful refinement was achieved in space group $P\bar{1}$. Diffraction data were

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[1] (a) Rutgers University, New Brunswick. (b) Rutgers University, Newark.

[2] Walshe, J. M. *Proc. R. Soc. Med.* **1977**, *70* (*Suppl. 3*), 1–3.

[3] Harders, H.; Cohnen, E. *Proc. R. Soc. Med.* **1977**, *70* (*Suppl. 3*), 10–2.

[4] Borthwick, T. R.; Benson, G. D.; Schugar, H. J. *Proc. Soc. Exp. Biol. Med.* **1979**, *162*, 227–8.

[5] We have adopted the shorthand nomenclature where linear tetraamines are characterized by the number of CH$_2$ units in each bridge. See ref 6.

[6] Weatherburn, D. C.; Billo, E. J.; Jones, J. P.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 1557–9.

[7] Van Alphen, J. *Recl. Trav. Chim. Pays-Bas* **1936**, *55*, 835–40.

[8] In addition to local programs for the IBM 370/168 computer, local modifications of the following programs were employed: LPCOR Lp and absorption program; Zalkin's FORDAP Fourier program; Johnson's ORTEP II thermal ellipsoid plotting program; Busing, Martin, and Levy's ORFFE error function program; Main, Lessinger, Declercq, Woolfson, and Germain's MULTAN 74 program for the automatic solution of crystal structures; the FLINUS least-squares program obtained from Brookhaven National Laboratories.

Table I. Crystal Data and Data Collection Details

formula	$Cu(C_7N_4H_{20})(ClO_4)_2$
mol wt	422.8
a, Å	12.996 (9)
b, Å	8.297 (2)
c, Å	8.549 (4)
α, deg	113.11 (3)
β, deg	83.93 (5)
γ, deg	113.37 (4)
space group	$P\bar{1}$
no. reflctns used to determine cell const	15
Z	2
d_{calcd}, g/cm³	1.807
d_{obsd}, g/cm³	1.808 (5)
λ, Å (Mo Kα)	0.710 69
monochromator	graphite crystal
linear abs coeff, cm⁻¹	18.4
cryst size, mm	0.40 × 0.10 × 0.14
abs factor range	1.19–1.73
diffractometer	Syntex P2₁
data collection method	θ–2θ
2θ limit, deg	55
scan rate, deg/min	2
scan range, deg	$2\theta(K\alpha_1) - 0.8$ to $2\theta(K\alpha_2) + 0.85$
no. of std reflctns	3
variation in std intens	4%
no. of unique reflctns collected	4556
no. of unique reflctns used (3σ)	2162
data:parameter ratio	10.9
final R_F	0.044
final R_{wF}	0.061

collected by using a crystal of dimensions 0.40 × 0.10 × 0.14 mm mounted parallel to the a axis on a glass fiber. Unit cell constants were determined by a least-squares fit of 15 moderately intense, high-angle reflections centered on a Syntex P2₁ diffractometer. A density of 1.807 g/cm³, calculated for two $Cu(C_7H_{20}N_4)(ClO_4)_2$ units per cell, is in close agreement with the value of 1.808 (5) g/cm³ measured by flotation in a mixture of $BrCH_2CH_2Br$ and CH_3OH.

Intensities, I, and their estimated standard deviations, $\sigma(I)$, were calculated from $I = (P - LB - HB)(SR)$ and $\sigma(I) = (P + LB + HB)^{1/2}(SR)$ where P is the peak count, LB is the low-angle background count, HB is the high-angle background count, and SR is the scan rate. Intensities were corrected for decay by applying average decay factors obtained from the standard reflections. All data were corrected for Lorentz, polarization, and absorption effects. Values for $\sigma(F_o^2)$ were computed from $\sigma(F_o^2) = (Lp)^{-1}(\sigma^2(I) + (0.03I)^2)^{1/2}$.

3. Solution and Refinement of the Structure.[8] The structure was solved by direct methods by using the program MULTAN 74 and refined by full-matrix, least-squares techniques. Neutral atom scattering factors from ref 9a were used. Both real and imaginary parts of the anomalous dispersion corrections were applied to Cu and Cl atoms.[9b] An E map, calculated by using 192 phases from the starting set having the highest combined figure of merit, revealed all but eight (two C and six O) nonhydrogen atoms; these were located readily on a subsequent difference electron density map. With all nonhydrogen scattering matter present, the initial agreement factor $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.229. Several cycles of isotropic refinement, based on F, led to convergence with $R_F = 0.097$.

At this point, H atoms were added to the model as fixed contributions to the structure factors. Methylene and amine H coordinates were calculated by assuming tetrahedral geometry with C–H and N–H distances of 0.95 and 0.87 Å, respectively.[10] All 20 H atoms were located in regions of high electron density in a difference Fourier map. Hydrogen atoms were assigned temperature factors according to $B_H = B_n + 1$ where n is the atom to which H is bonded. H atom parameters were not refined.

Several additional cycles of refinement of coordinates and anisotropic temperature factors for all nonhydrogen atoms, using unit weights, reduced R_F to 0.044 and $R_{wF} = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ to 0.061. For the final cycle, all parameter changes were within 0.1σ, where σ is the esd obtained from the inverse matrix. A final difference map showed a general background of approximately ±0.20 e/Å³. The largest positive peak (0.29 e/Å³) was smaller than the largest negative peak. Final atomic parameters are listed in Table II. Views of the complex and its packing are shown in Figures 1 and 2, respectively. A list of observed and calculated structure factors is available.[11]

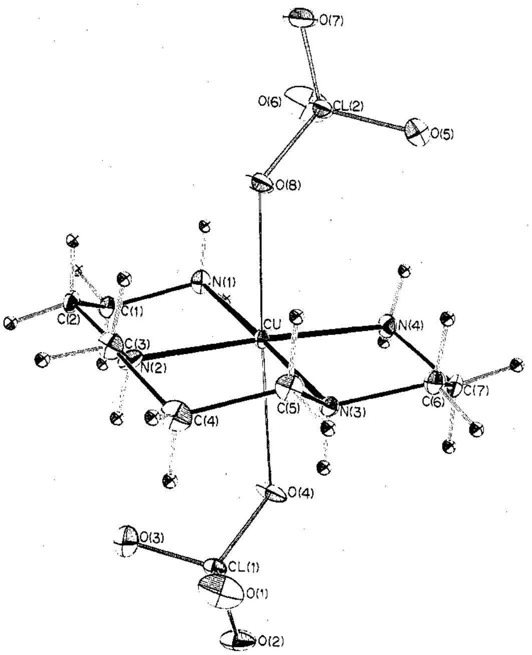

Figure 1. View of $Cu(2,3,2\text{-tet})(ClO_4)_2$ showing the atom numbering scheme.

Discussion

The effectiveness of 2,3,2-tet in inducing the excretion of copper from rats[4] presumably results from the stability of the $Cu(2,3,2\text{-tet})^{2+}$ complex. Stability constants (Table III) for a series of Cu(II) complexes with 2,2,2-tet, 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet ligands span the range $10^{17.3}$ to $10^{23.9}$.[6,12] Published thermodynamic data (Table III) show that this variation originates primarily from differences in the enthalpy of complex formation. Empirical force-field calculations[14] suggest that differences in the enthalpies of formation of Ni(II)–tetraamine complexes arise mainly from valence angle deformations and nonbonded interactions, with minor contributions from torsional strain and bond elongations. Similar structural considerations should also account for the varying stabilities of the Cu(II)–tetraamine complexes. Accordingly, structural features of the title complex will be compared with those reported for other Cu(II) tetraamines and reference Cu(II)–diamine complexes. To facilitate this comparison, preliminary structural data for $Cu(3,3,3\text{-tet})(ClO_4)_2$ will also be utilized.[15]

The structure of the title complex (Figure 1) consists of Cu(II) monomers with tetragonal N_4O_2 ligand donor sets.

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(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 71–98; (b) pp 148–51.

(10) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–4.

(11) Supplementary material.

(12) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *J. Chem. Soc., Dalton Trans.* **1978**, 577–83 and references therein.

(13) Bianchini, C.; Fabbrizzi, L.; Paoletti, P.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 197–9.

(14) McDougall, G. J.; Hancock, R. D.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1438–44.

(15) $Cu(C_8H_{22}N_4)(ClO_4)_2$ crystallizes in the orthorhombic space group *Pbca* with $a = 15.765$ (5) Å, $b = 15.323$ (5) Å, $c = 14.523$ (5) Å, $d_{obsd} = 1.69$ (1) g/cm³, $d_{calcd} = 1.710$ g/cm³, and $Z = 4$. The structure contains tetragonal CuN_4O_2 units which are similar to those in the title complex, but somewhat distorted (see text). Of the two unique perchlorate groups in the structure, one is not bound to copper. The second perchlorate group, which bridges symmetry-related copper atoms and accounts entirely for the axial coordination, is disordered. At the current stage of refinement using 1658 reflections, the conventional R factor is 0.118.

Table II. Fractional Atomic Coordinates and Thermal Parameters[a,b] for Cu(2,3,2-tet)$(ClO_4)_2$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.78353 (7)	0.8392 (1)	0.7942 (1)	27.6 (6)	7.5 (2)	7.4 (1)	15.7 (7)	6.3 (6)	2.5 (1)
Cl(1)	0.8521 (1)	0.6702 (2)	1.0819 (2)	37 (1)	12.6 (4)	10.7 (3)	13 (2)	−7 (1)	6.4 (3)
Cl(2)	0.7137 (2)	1.0182 (3)	0.5300 (2)	64 (2)	11.8 (4)	12.6 (3)	22 (2)	−13 (2)	7.1 (3)
O(1)	0.7346 (5)	0.5974 (11)	1.0935 (11)	35 (5)	39 (2)	39 (2)	10 (8)	10 (8)	25 (2)
O(2)	0.9111 (5)	0.7084 (10)	1.2325 (8)	83 (6)	29 (2)	15 (1)	20 (8)	−37 (6)	14 (1)
O(3)	0.8809 (7)	0.5335 (10)	0.9413 (9)	17 (1)	27 (2)	18 (1)	139 (12)	27 (9)	5 (1)
O(4)	0.8889 (5)	0.8422 (8)	1.0472 (8)	73 (5)	16 (1)	21 (1)	1 (7)	−37 (6)	13 (1)
O(5)	0.6922 (8)	1.1587 (10)	0.6732 (9)	242 (12)	23 (2)	16 (1)	167 (13)	−2 (10)	5 (1)
O(6)	0.8317 (6)	1.0874 (13)	0.5082 (13)	56 (6)	42 (3)	50 (3)	13 (10)	17 (10)	33 (2)
O(7)	0.6518 (6)	0.9826 (9)	0.3836 (8)	115 (7)	23 (2)	17 (1)	37 (9)	−45 (7)	12 (1)
O(8)	0.6812 (5)	0.8468 (8)	0.5633 (7)	78 (5)	13 (1)	17 (1)	19 (6)	−22 (6)	10 (1)
N(1)	0.9174 (5)	0.8463 (8)	0.6488 (8)	39 (5)	12 (1)	12 (1)	20 (6)	12 (6)	4 (1)
N(2)	0.7265 (5)	0.5540 (8)	0.6676 (7)	33 (4)	9 (1)	8 (1)	12 (6)	−2 (5)	4 (1)
N(3)	0.6500 (5)	0.8277 (8)	0.9425 (7)	40 (4)	11 (1)	8 (1)	33 (6)	9 (5)	4 (1)
N(4)	0.8432 (5)	1.1215 (8)	0.9328 (8)	50 (5)	9 (1)	10 (1)	13 (6)	7 (6)	3 (1)
C(1)	0.9165 (7)	0.6520 (11)	0.5712 (10)	58 (6)	17 (2)	11 (1)	66 (9)	24 (7)	6 (1)
C(2)	0.7954 (7)	0.5176 (10)	0.5175 (9)	70 (7)	11 (2)	7 (1)	38 (8)	22 (7)	3 (1)
C(3)	0.6014 (6)	0.4536 (10)	0.6718 (10)	34 (5)	11 (2)	13 (1)	−2 (7)	−19 (7)	4 (1)
C(4)	0.5334 (6)	0.4889 (11)	0.7717 (11)	27 (5)	13 (2)	17 (2)	−8 (7)	−4 (7)	7 (1)
C(5)	0.5378 (6)	0.6906 (11)	0.8562 (10)	26 (5)	17 (2)	14 (1)	23 (8)	6 (7)	8 (1)
C(6)	0.6537 (6)	1.0235 (11)	1.0280 (9)	57 (6)	16 (2)	10 (1)	61 (9)	22 (7)	5 (1)
C(7)	0.7762 (7)	1.1576 (11)	1.0836 (9)	76 (7)	12 (2)	8 (1)	50 (9)	17 (7)	2 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H1(N1)	0.912	0.884	0.568	2.8	H1(N4)	0.913	1.161	0.965	2.8
H2(N1)	0.979	0.925	0.710	2.8	H2(N4)	0.837	1.180	0.871	2.8
H1(N2)	0.740	0.507	0.734	2.3	H1(C1)	0.961	0.640	0.475	3.2
H1(N3)	0.660	0.794	1.022	2.4	H2(C1)	0.944	0.625	0.652	3.2
H1(C2)	0.789	0.389	0.475	3.0	H1(C5)	0.482	0.694	0.936	3.0
H2(C2)	0.769	0.539	0.430	3.0	H2(C5)	0.523	0.727	0.770	3.0
H1(C3)	0.583	0.321	0.559	2.9	H1(C6)	0.609	1.033	1.124	2.8
H2(C3)	0.584	0.501	0.542	2.9	H2(C6)	0.626	1.056	0.950	2.8
H1(C4)	0.563	0.464	0.854	3.3	H1(C7)	0.783	1.286	1.128	3.1
H2(C4)	0.458	0.404	0.740	3.3	H2(C7)	0.801	1.134	1.169	3.1

[a] Values for β_{22}, β_{33}, and β_{23} are $\times 10^3$; all other values are $\times 10^4$. [b] The form of the anisotropic thermal ellipsoid is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

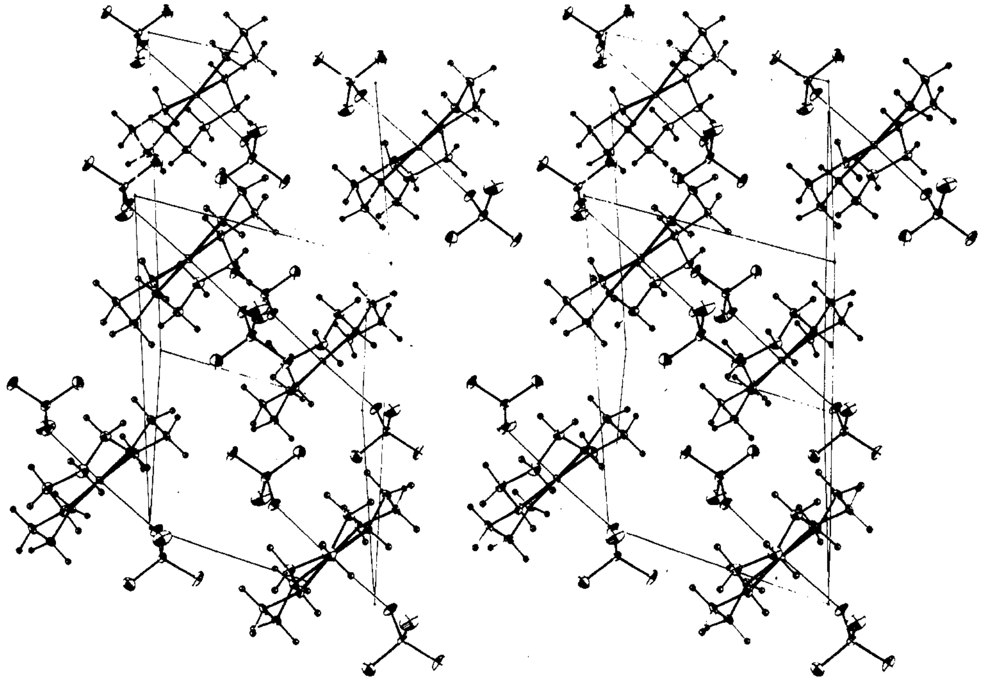

Figure 2. Stereoscopic packing diagram for Cu(2,3,2-tet)$(ClO_4)_2$ viewed approximately along $\bar{b}$. The c axis is approximately horizontal and the $\bar{a}$ axis vertical.

Bond distances and angles are listed in Table IV. Equatorial N_4 ligation is provided by the 2,3,2 tetraamine, while apical Cu–O bonds result from coordination of two monodentate perchlorate groups.

The observed Cu–O bond lengths of 2.667 (5) and 2.527 (5) Å differ significantly; the longer length just falls within the range of 2.575 (6)–2.676 (10) Å in related complexes containing CuN_4O_2 chromophores (Table V) while both lengths are within the range of 2.52 (2)–2.883 (2) Å reported[22]

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(16) Brown, D. S.; Lee, J. D.; Melsom, B. G. A. *Acta Crystallogr., Sect. B* **1968**, *24*, 730–4.

Table III. Selected Spectroscopic and Thermodynamic Data for $(Cu\text{-tetraamine})^{2+}$ Complexes

complex	log *K*	ΔH_f, kcal mol^{-1}	ΔS, eu	λ_{max}, cm^{-1}	ref
$Cu(2,2,2\text{-tet})^{2+}$	20.2	−21.6	19.5	17 240	6, 12, 13
$Cu(2,3,2\text{-tet})^{2+}$	23.9	−27.7	16.5	18 940	6, 12, 13
$Cu(3,2,3\text{-tet})^{2+}$	21.8	−25.5	13.1	18 400	12, 13
$Cu(3,3,3\text{-tet})^{2+}$	17.3	−19.5	12.8	16 750	6, 12, 13

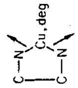
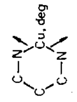
Table IV. Bond Distances (Å) and Angles (Deg) for $Cu(2,3,2\text{-tet})(ClO_4)_2$

Distances			
Cu-N(1)	2.024 (6)	C(5)-N(3)	1.489 (9)
Cu-N(2)	2.022 (6)	N(3)-C(6)	1.479 (9)
Cu-N(3)	2.032 (6)	C(6)-C(7)	1.53 (1)
Cu-N(4)	2.016 (6)	C(7)-N(4)	1.476 (9)
Cu-O(4)	2.667 (5)	Cl(1)-O(1)	1.411 (6)
Cu-O(8)	2.527 (5)	Cl(1)-O(2)	1.428 (5)
N(1)-C(1)	1.478 (9)	Cl(1)-O(3)	1.429 (7)
C(1)-C(2)	1.51 (1)	Cl(1)-O(4)	1.454 (5)
C(2)-N(2)	1.486 (9)	Cl(2)-O(5)	1.415 (7)
N(2)-C(3)	1.520 (8)	Cl(2)-O(6)	1.428 (7)
C(3)-C(4)	1.50 (1)	Cl(2)-O(7)	1.427 (6)
C(4)-C(5)	1.52 (1)	Cl(2)-O(8)	1.448 (5)

Angles			
N(1)-Cu-N(2)	85.3 (2)	Cu-N(3)-C(6)	107.4 (4)
N(2)-Cu-N(3)	93.9 (2)	N(3)-C(6)-C(7)	107.7 (6)
N(3)-Cu-N(4)	85.2 (2)	C(6)-C(7)-N(4)	107.9 (6)
N(1)-Cu-N(3)	178.5 (4)	Cu-N(4)-C(7)	108.5 (4)
N(2)-Cu-N(4)	176.4 (3)	Cu-O(4)-Cl(1)	118.9 (3)
O(4)-Cu-O(8)	177.6 (2)	Cu-O(8)-Cl(2)	121.1 (3)
O(4)-Cu-N(1)	91.8 (2)	Cu-N(1)-C(1)	108.1 (4)
O(4)-Cu-N(2)	94.6 (2)	N(1)-C(1)-C(2)	106.6 (6)
O(4)-Cu-N(3)	86.9 (2)	C(1)-C(2)-N(2)	108.7 (6)
O(4)-Cu-N(4)	82.0 (2)	N(2)-C(3)-C(4)	111.1 (6)
O(8)-Cu-N(1)	89.8 (2)	C(2)-N(2)-C(3)	112.0 (6)
O(8)-Cu-N(2)	87.3 (2)	Cu-N(2)-C(2)	106.8 (4)
O(8)-Cu-N(3)	91.4 (2)	C(3)-C(4)-C(5)	115.0 (6)
O(8)-Cu-N(4)	96.2 (2)	C(4)-C(5)-N(3)	111.7 (6)
O(1)-Cl(1)-O(2)	112.3 (4)	C(5)-N(3)-C(6)	111.8 (6)
O(1)-Cl(1)-O(3)	108.7 (5)	Cu-N(3)-C(5)	116.3 (5)
O(1)-Cl(1)-O(4)	110.4 (4)	O(5)-Cl(2)-O(6)	107.8 (6)
O(2)-Cl(1)-O(3)	108.5 (4)	O(5)-Cl(2)-O(7)	109.2 (4)
O(3)-Cl(1)-O(4)	107.1 (4)	O(5)-Cl(2)-O(8)	108.9 (4)
O(2)-Cl(1)-O(4)	109.7 (3)	O(6)-Cl(2)-O(7)	111.1 (5)
		O(6)-Cl(2)-O(8)	108.9 (4)
		O(7)-Cl(2)-O(8)	110.8 (3)

for a variety of copper(II) complexes containing coordinated perchlorate groups. As indicated by the Cl–O distances, the perchlorate groups exhibit effective C_{3v} symmetry. The Cl(1)–O(4) and Cl(2)–O(8) bond lengths are significantly longer than the remaining Cl–O distances which are equivalent within experimental error. A similar lengthening has been observed in a structural study of $Cu(NH_2CH_2CH_2SCH_3)_2(ClO_4)_2$ and reasonably may be attributed to the ligand rôle of the O(4) and O(8) atoms.[24] Distortions of the perchlorate groups from T_d symmetry are not mirrored in the O–Cl–O angles which range randomly from 107.1 (4) to 112.3 (4)° and average to 109.5°.

Table V. Selected Structural Data for Cu(II)-Tetraamine and -Diamine Complexes

	$Cu(en)_2(BF_4)_2$	$Cu(L^a)_2(ClO_4)_2$	$Cu(Pn)_2(ClO_4)_2$	$Cu(L^b)_2(ClO_4)_2$	$Cu(L^b)_2(ClO_4)_2$	$Cu(L^c)_2(NO_2)_2$	$Cu(2,2,2\text{-tet})(SCN)_2$	$Cu(2,3,2\text{-tet})(ClO_4)_2$	$Cu(3,4,3\text{-tet})(ClO_4)_2$	$Cu(3,3,3\text{-tet})(ClO_4)_2$	$Cu(cyclam^d)(ClO_4)_2$
Cu-N, Å	2.02 (1)–2.03 (1)	2.004 (5)–2.066 (5)	2.01 (3)–2.03 (3)	2.027 (7)–2.031 (7)	2.018 (6)–2.037 (6)	2.028 (6)–2.048 (6)	2.008 (7)–2.030 (5)	2.016 (6)–2.032 (6)	2.008 (8)–2.062 (8)	2.02 (2)–2.04 (2)	2.02 (2), 2.02 (4)
	86.4 (5)	84.6 (2)	86.0				84.6 (3) 84.3 (2) 84.7 (3)	85.3 (2) 85.2 (2)			86.0 (2)
				93.3 (2)	88.9 (3)	86.8 (2)		93.9 (2)	94.6 91.1	92.7 (7) 97.7 (7) 85.3 (7)	94.0 (2)
trans N-Cu-N, deg	180[e]	180[e]	180[e]	180[e]	180[e]	180[e]	154.0 161.0	176.4 (3) 178.5 (4)	159.3 172.7	159.4 (7) 169.4 (7)	180[e]
Cu-L(apical), Å	2.56 (1)	2.575 (6)	2.61 (2)	2.676 (10)	2.579 (6)	2.655 (8)	2.607 (2)	2.667 (5) 2.527 (5)			2.57 (4)
ref	16	17	18	19	19	20	21	this work	23	15	22
comments	gauche	gauche	gauche	chair, form A	chair, form B	chair	gauche, gauche, gauche; Cu 0.4 Å from CuN_4 plane	see text	see text	see text	gauche, chair

[a] $CH_3NHCH_2NH_2$. [b] $H_2NCH_2CH_2CH(NH_2)CH_3$. [c] $H_2N(CH_2)_3NH_2$. [d] $(\text{-}NH(CH_2)_3NH(CH_2)_2\text{-})_2$. [e] Required by symmetry and yielding planar CuN_4 units.

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Table VI. Possible Hydrogen Bonds in $Cu(2,3,2\text{-tet})(ClO_4)_2$

donor (D)	hydrogen (H)	acceptor (A)[a]	D–H···A, deg	D···A, Å	H···A, Å	D–H, Å
N(1)	H1(N1)	$O(2)^{i}$	129	3.282 (9)	2.66	0.88
N(1)	H1(N1)	$O(6)^{ii}$	141	3.26 (1)	2.53	0.88
N(2)	H1(N2)	$O(3)^{ii}$	147	3.33 (1)	2.57	0.87
N(2)	H1(N2)	$O(5)^{iii}$	128	3.149 (8)	2.54	0.87
N(3)	H1(N3)	$O(1)^{ii}$	146	3.23 (1)	2.47	0.87
N(4)	H2(N4)	$O(5)^{ii}$	140	3.29 (1)	2.57	0.87
N(1)	H2(N1)	$O(2)^{iv}$	126	3.263 (8)	2.66	0.88
N(1)	H2(N1)	$O(4)^{iv}$	163	3.274 (7)	2.44	0.88
N(4)	H2(N4)	$O(3)^{v}$	131	3.228 (12)	2.58	0.87
N(4)	H1(N4)	$O(4)^{iv}$	156	3.389 (10)	2.58	0.87

[a] The following symmetry operators relate the acceptor to the donor atoms: i = $x, y, z - 1$; ii = x, y, z; iii = $x, y - 1, z$; iv = $2 - x, 2 - y, 2 - z$; v = $x, y + 1, z$.

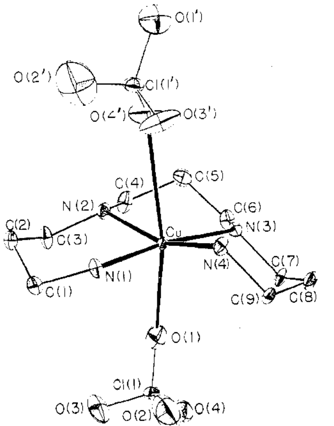

Figure 3. View of $Cu(3,3,3\text{-tet})(ClO_4)_2$ showing the nonhydrogen atoms. Only the bridging perchlorate group is shown.[15]

As indicated by the Cu–O–Cl angles of 118.9 (3) and 121.1 (3)°, the perchlorate groups are tilted substantially with respect to the CuN_4 plane, an effect which has been noticed previously.[22,24] Although the temperature factors of the perchlorate oxygen atoms are approximately twice as large, on the average, as those of the ligand carbon and nitrogen atoms, the perchlorate groups appear well-behaved and show no apparent signs of disorder, possibly as a result of weak, intra- and intermolecular hydrogen bonds to several –NH and $-NH_2$ donor groups (Table VI).

The Cu–N bond distances span the rather narrow range 2.016 (6)–2.032 (6) Å, while the CuN_4 chromophore is planar to ±0.03 Å (Table VII). These Cu–N distances are typical for Cu(II) complexes of polyamines (Table V). As indicated by the data in Table V, Cu–N bond distances are relatively insensitive to ring strain and/or deviations of the CuN_4 units from planarity for this series of complexes. For example, the Cu–N distances in both $Cu(2,2,2\text{-tet})(SCN)_2$[21] and $Cu(3,3,3\text{-tet})(ClO_4)_2$[15] lie in the range of 2.02–2.04 Å even though the Cu atom lies 0.4 Å from the N_4 plane of the 2,2,2-tet ligand and the CuN_4 unit in the Cu(3,3,3-tet) complex is quite irregular (Figure 3). For the largest homologue of this series, $Cu(3,4,3\text{-tet})(ClO_4)_2$, ring strain apparently has begun to affect the Cu–N bond distances. The Cu–N distances involving terminal ligand atoms are 2.008 and 2.019 Å, whereas those involving the inner nitrogen donors are 2.049 and 2.062 Å.

Referring to the bis(diamine)copper(II) complexes in Table V, nonconsecutive five-membered chelate rings adopt the stable gauche configuration and corresponding six-membered rings adopt the stable chair configuration, while the CuN_4 chromophores are planar. With the Cu(II)–tetraamine complexes, ring conformation and CuN_4 planarity depend upon the size of the linked chelate rings. For example, other workers have utilized molecular models to predict that the three linked five-membered rings of metal 2,2,2-tet complexes cannot all have the gauche conformation if the MN_4 unit is to be planar. Thus, the central five-membered ring has the eclipsed conformation in the planar NiN_4 unit of the $Ni(2,2,2\text{-tet})^{2+}$ complex,[25] while all three rings are gauche in the analogous $Cu(2,2,2\text{-tet})^{2+}$ unit, but the Cu atom is displaced 0.4 Å from the N_4 plane.[21] Apparently, the cumulative ring strain is too great to allow copper to lie in the center of the N_4 plane, and the stable gauche arrangements of these chelate rings are formed with some accompanying sacrifice of Cu(II)–ligand overlap. In contrast, the $Cu(2,3,2\text{-tet})^{2+}$ complex has a nearly planar CuN_4 unit (Table VII) in which alternate five-, six-, and five-membered chelate rings have the stable gauche, chair, and gauche conformations, respectively. In the $Cu(3,3,3\text{-tet})^{2+}$ complex, all three six-membered rings have the stable chair conformation, but the CuN_4 unit is distorted; as with the $Cu(2,2,2\text{-tet})^{2+}$ complex, stable chelate ring configurations are obtained at the expense of Cu(II)–ligand overlap.

Table VII. Least-Squares Planes and Deviations Therefrom for $Cu(2,3,2\text{-tet})(ClO_4)_2$

Equations of the Planes[a]

plane	*A*	*B*	*C*	*D*	atoms defining plane
I	0.4252	−0.6069	0.6715	7.8740	Cu, N(1), N(2), N(3), N(4)
II	0.3300	−0.6346	0.6988	7.1448	Cu, N(1), N(2), C(1), C(2)
III	0.3254	−0.6734	0.6638	6.8947	Cu, N(3), N(4), C(6), C(7)
IV	−0.1383	−0.8058	0.5758	2.9640	N(2), N(3), C(3), C(5)

Deviations from the Planes (Å)

	atom	dev, Å		atom	dev, Å
I	Cu	−0.0283	II	Cu	0.0094
	N(1)	−0.0087		N(1)	−0.1562
	N(2)	0.0229		N(2)	0.1377
	N(3)	−0.0089		C(1)	0.2901
	N(4)	0.0230		C(2)	−0.2810
III	Cu	−0.0101	IV	Cu	−0.8249
	N(3)	0.1595		N(2)	0.0002
	N(4)	−0.1356		N(3)	−0.0002
	C(6)	−0.2900		C(3)	−0.0003
	C(7)	0.2762		C(4)	0.7333
				C(5)	0.0003

[a] Equations are in the form of $AX_0 + BY_0 + CZ_0 = D$ where X_0, Y_0, and Z_0 are Cartesian axes lying along $b \times c^*$, b, and c^*, respectively.

Differences in Cu(II)–ligand interactions for the Cu(II)–tetraamine complexes are reflected[13] in their enthalpies of formation, in the position of their ligand field bands, and in their stability constants. For the complexes listed in Table III, a one-to-one correspondence exists between these three properties. Within the $Cu(2,3,2\text{-tet})^{2+}$ unit, the N–Cu–N bond angles [178.5 (4), 176.4 (3)°] are close to 180° and the CuN_4 group is almost planar. Consequently, the N_4 donor set in this complex nearly matches the symmetry properties of the Cu(II) orbitals; on this basis, a relatively stable complex is expected (and found). Deviations of the homologous, crystallographically characterized $Cu(2,2,2\text{-tet})^{2+}$ and $Cu(3,3,3\text{-tet})^{2+}$ complexes from this idealized bonding arrangement are reflected by the thermodynamic and spectroscopic data in Table III. For example, $Cu(3,3,3\text{-tet})^{2+}$, with a distorted CuN_4 unit and N–Cu–N angles of 159.4 (7) and 169.4 (7)°, has a stability constant which is some $10^{6.6}$ times smaller than that for $Cu(2,3,2\text{-tet})^{2+}$.

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In view of the above considerations, the arrangement of the 2,3,2-tet ligand in the title complex appears to be relatively strain free and to lead to strong Cu(II)–ligand overlap. Closure of the 2,3,2-tet ligand with a $-(CH_2)_3-$ bridge yields a 2,3,2,3 macrocyclic tetraamine whose metal complexes contain linked 5,6,5,6 arrangements of chelate rings. Cu(cyclam)$^{2+}$ and Cu(tet-a)$^{2+}$ are examples of such systems. These and related macrocyclic complexes exhibit exceptional stability ($\log K \sim 28$)[12,26] and blue-shifted ligand field bands. In Cu(cyclam)$^{2+}$, the Cu–N distances, N–Cu–N angles, planarity of the CuN_4 chromophores, and configurations of the chelate rings closely resemble those of the title complex (Table V). The relatively high stability of the Cu(2,3,2-tet)$^{2+}$ complex is consistent with its close structural relationship to the Cu(cyclam)$^{2+}$ complex.

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Registry No. Cu(2,3,2-tet)$(ClO_4)_2$, 72331-56-7.

Supplementary Material Available: A listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Aromatic Thiolato Complex (2-Mercaptoaniline-*N*,*S*)bis(ethylenediamine)cobalt(III). Crystal Structure of $[(en)_2Co(SC_6H_4NH_2)](ClO_4)Cl$

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The aromatic thiolato complex $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ may be synthesized by reduction of $[o\text{-}C_6H_4(NH_2)S-]_2$ with an ethylenediamine–cobalt(II) mixture in a water–tetrahydrofuran solvent system. This complex is shown to undergo the same oxidation, alkylation, and adduct formation reactions characteristic of the aliphatic thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. The visible–UV spectrophotometric parameters of the aliphatic and aromatic analogues, and those of their derivatives, are compared and discussed. The title complex crystallizes in space group $P2_1/n$ with $a = 9.904$ (1) Å, $b = 7.5045$ (8) Å, $c = 23.308$ (2) Å, $\beta = 92.693$ (8)°, and $Z = 4$. A total of 2543 unique reflections measured with an automated diffractometer were used to refine the crystal structure to a conventional R factor of 0.035. The cobalt atom is octahedrally coordinated by five nitrogen atoms and the sulfur atom of the *o*-mercaptoaniline ligand, all six ligand–metal bond lengths being equivalent to the analogous bond lengths observed in $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. The cobalt(III) coordination sphere therefore appears to be structurally indifferent to the distinction between aromatic and aliphatic thiolato ligands. The best current estimate of the thiolato-induced structural trans effect is 0.044 (2) Å.

Introduction

The 1-equiv reduction of an organic disulfide (or diselenide) by a labile metal(II) center to yield an inert thiolato- (or selenolato-) metal(III) complex has proven to be an important and useful synthetic route to the general class of robust metal–chalcogen complexes.[3-9]

$$2M^{II} + RXXR \rightarrow 2M^{III}\text{–}XR \qquad (1)$$

$$X = S, Se$$

We have been particularly interested in chelated (thiolato)bis(ethylenediamine)cobalt(III) complexes as advantageous substrates on which to base investigations of the sulfur-induced structural trans effect,[10-12] the properties and reactivity of coordinated sulfur,[10-15] and the ability of sulfur to mediate inner-sphere electron transfer.[6,16,17] These complexes are readily prepared in aqueous media by reaction 1 when RSH is an *aliphatic* thiol containing a suitable chelate functionality, e.g.

$$4en + 2Co^{2+}(aq) + [H_2NCH_2CH_2S-]_2 \rightarrow 2[(en)_2Co(SCH_2CH_2NH_2)]^{2+} \qquad (1a)$$

However, this preparation is not nearly so straightforward when RSH is an *aromatic* chelating thiol (e.g., $o\text{-}C_6H_4(NH_2)SH$ rather than $NH_2CH_2CH_2SH$), and until this study the preparation of an aromatic (thiolato)bis(ethylenediamine)cobalt(III) complex by eq 1 had not succeeded. The difficulties encountered in applying eq 1a to aromatic systems could arise from the undoubtedly complicated, multistep, redox

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