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Crystal and Molecular Structure of the Novel Mixed-Valence Complex μ-Bis(*N*,*N*-diethyldithiocarbamato)-bis(*N*,*N*-diethyldithiocarbamato)-dicarbonyldiruthenium(II,III) Tetrafluoroborate, $[Ru_2(Et_2dtc)_4(CO)_2]BF_4$

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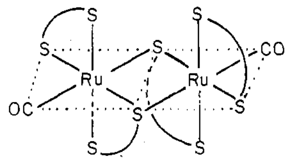
Received July 30, 1979

Slow electrochemical oxidation of bis[bis(*N*,*N*-diethyldithiocarbamato)carbonylruthenium(II)], $[Ru(dtc)_2CO]_2$ (**1**), in CH_2Cl_2 solution at 25 °C yields the novel mixed-valence Ru(II, III) complex $[Ru_2(dtc)_4(CO)_2]^+$ (**2**). A single-crystal X-ray analysis of the tetrafluoroborate salt of **2** has been carried out by using automatic diffractometer data. The triclinic space group $A\bar{1}$ was chosen with unit cell dimensions of $a = 17.451$ (4) Å, $b = 26.43$ (1) Å, $c = 16.757$ (4) Å, $\alpha = 101.26$ (3)°, $\beta = 87.80$ (2)°, $\gamma = 85.18$ (3)°, and $Z = 4$, assuming the asymmetric unit to contain $Ru_4S_{16}C_{44}H_{80}N_8O_4B_2F_8$. The final R value using 6789 observations and 497 variables was 0.047. The asymmetric unit contains two crystallographically nonequivalent $[Ru_2(dtc)_4(CO)_2]BF_4$ molecules. The most important feature of the structure is the cis arrangement of the CO ligands which are both coordinated to the same Ru atom. Since the compound was synthesized from **1** which has a trans CO structure with one CO on each Ru atom, the oxidation reaction has resulted in an unusual CO rearrangement. Each Ru atom is six-coordinate and the structure is best described as a bis chelated $Ru(dtc)_2$ moiety sharing two S atoms (bridging) of different dtc ligands of a six-coordinate $Ru(dtc)_2(CO)_2$ moiety. The Ru–S (bridging) distances (average 2.454 (2) Å) are longer than the Ru–S(nonbridging) distances (average 3.369 (2) Å), and the Ru–Ru distance of 3.614 (1) Å indicates no significant rutnenium–ruthenium bonding.

Introduction

A number of bimetallic dithiocarbamato (dtc) complexes have recently been characterized by single-crystal X-ray techniques.[1-7] Interest in these compounds stems from their novel structural[1-7] and electrochemical properties[8,9] and more recently from their photoredox chemistry.[10,11] Additionally, metal dithiocarbamato complexes have been shown to be effective accelerators in the vulcanization of rubber,[12,13] and the recent characterization of a bimetallic trithiocarbamate complex of osmium is important.[6] Not much work has been done with mixed dtc carbonyl complexes although such compounds are expected to have interesting electrochemical and photochemical properties. Raston and White[7] recently showed that the complex $Ru(Et_2dtc)_2CO$, originally synthesized by Kingston and Wilkinson,[16] is actually dimeric in the solid state. The structure of $[Ru(Et_2dtc)_2CO]_2$ was determined by single-crystal X-ray analysis and is shown in structure **1**.[7] This complex is also dimeric in noncoordinating solvents such as CH_2Cl_2.[7,17] An electrochemical study of **1** in CH_2Cl_2 solution was undertaken in order to see if the CO ligands would be lost upon oxidation, thus producing reactive species which should lead to new bimetallic complexes. Surprisingly, electrochemical oxidation of **1** in CH_2Cl_2 solution yielded a new dicarbonyl mixed-valence Ru(II)–Ru(III) complex $[Ru(Et_2dtc)_4(CO)_2]^+$ (**2**) which was isolated in high yield as a tetrafluoroborate salt. The structure of **2** has been determined by single-crystal X-ray analysis (vide infra). The details of the electrochemistry of **1** and its oxidation product, **2**, are complicated and will be described in a future publication.[17]



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Experimental Section

Preparation of $[Ru_2(Et_2dtc)_4(CO)_2]BF_4$. This complex was prepared by *slow* controlled potential oxidation (25 °C, for at least 12 h) of **1**[7,16] (ca. 10^{-3} M) in CH_2Cl_2 solution ca. 0.2 M in tetrabutylammonium tetrafluoroborate (TBAF) at 1.3 V vs. SCE. The dark green product was chromatographed three times by using silica gel columns and eluents consisting of 5, 7.5, and 10% acetone in CH_2Cl_2 (v/v), respectively, for the three successive elutions. The repetitive chromatographies were needed in order to remove all of the TBAF supporting electrolyte. The complex was precipitated from the final eluent by adding heptane and removing the CH_2Cl_2 in vacuo. The yield was 60% after chromatography. The complex can also be prepared by a nonelectrochemical method. Boron trifluoride gas was bubbled through a CH_2Cl_2 solution of **1** (ca. 10^{-3} M) for 60 s. The solution was then purged with CO for 15 min and stored in a closed flask in the dark under an oxygen atmosphere for 12 h. The product was chromatographed by using a silica gel column and 10:90 volume percent acetone/CH_2Cl_2 as eluent and isolated as described above in 40% yield. Crystals of **2** were obtained by very slow (1.5–3 weeks) evaporation of a CH_2Cl_2–heptane solution of **2** at 0 °C. Finally, the crystals were washed with cold ethanol and heptane to remove a brown oily impurity.

Anal. Calcd for $Ru_2S_8C_{22}H_{40}N_4O_2BF_4$: C, 28.17; H, 4.30; N, 5.97. Found: C, 28.31; H, 4.26; N, 6.00. IR (thin film on salt plate): ν(CO) 2055, 1998 cm^{-1}; ν(C$\overset{..}{-}$N) 1521 cm^{-1}; ν(B–F) 1070 cm^{-1}. Conductivity (25 °C in CH_2Cl_2) 56 cm^2 Ω^{-1} equiv^{-1}. Mp 165–167 °C. Magnetic data (solid state at 25 °C by Faraday method): $\chi_M^{corr} = 1082 \times 10^{-6}$ cgsμ/mol (diamagnetic correction 451 × 10^{-6} cgsμ/mol) giving μ_{eff} of 1.61 μ_B. Electronic absorption spectrum in CH_2Cl_2 solution: λ_{max} (log ϵ) 241 (4.67), 258 (4.62, sh), 411 (3.34, sh), 454 (3.20, sh), and 687 (3.30) nm.

Structure Determination. Single crystals of $[Ru_2(Et_2dtc)_4(CO)_2]BF_4$ were grown by slow evaporation from a dichloromethane–heptene solution. The dark green crystal used for data collection had four

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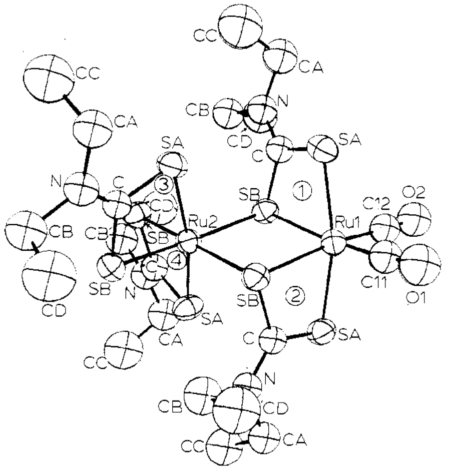

Figure 1. ORTEP drawing of the Ru1–Ru2 cation $[Ru_2(Et_2dtc)_4(CO)_2]^+$.

sets of parallel faces with interfacial distances of 0.48, 0.36, 0.36, and 0.16 mm. The *c* crystallographic axis was approximately parallel to the spindle axis. Precession photographs (Cu Kα radiation) suggested that the unit cell was triclinic, and the space group $A\bar{1}$ was chosen since it gave a cell closest to orthogonal which fit the crystal morphology. Successful solution and refinement of the structure confirmed the choice of a triclinic cell. The unit cell dimensions were determined by least-squares refinement of the angular settings of 25 Mo Kα (λ = 0.71069 Å) peaks centered on a CAD4 diffractometer[18a] at ambient temperature and are a = 17.451 (4) Å, b = 26.43 (1) Å, c = 16.757 (4) Å, α = 101.26 (3)°, β = 87.80 (2)°, γ = 85.18 (3)°, and V = 7541 (7) $Å^3$.[19] The structure was solved by using the $A\bar{1}$ space group[20] with Z = 4 giving a calculated density of 1.65 which agrees well with the measured density of 1.62 g cm^{-3}, assuming the asymmetric unit to contain $Ru_4S_{16}C_{44}H_{80}N_8O_4B_2F_8$. A total of 11 791 unique reflections were measured in the scan range 2θ = 0–50° on an Enraf-Nonius CAD4 automatic diffractometer using graphite monochromatized Mo Kα radiation and employing a variable rate ω–2θ scan technique.[18a] No decay was noted in the intensities of the three check reflections measured at intervals of 200 sequential reflections. After correction for Lorentz, polarization, background, and absorption (μ = 12.527 cm^{-1}) effects, 6789 reflections (58%) were judged observed ($F_o^2 \geq 4\sigma(F_o^2)$) and were used in all subsequent calculations.[18b] Conventional heavy-atom techniques were used to solve the structure, and refinement, with the 4 ruthenium, 16 sulfur, and 8 fluorine atoms thermally anisotropic and the remaining nonhydrogen atoms isotropic by full-matrix least-squares methods (497 variables), converged R and R_w to their final values of 0.047 and 0.063, respectively.[21] Two of the methyl carbon atoms were found to be disordered between two positions and, therefore, the multiplicities were refined in addition to the positional and thermal parameters for C6C, C6C′, C5D, and C5D′. The error in an observation of unit weight was 1.76, using a value of 0.05 for p in the $\sigma(I)$ equation.[18a] In the final difference Fourier, the highest peak was 1.7 e $Å^{-3}$ and was located close to F3 and F4. No new chemically significant features were apparent in the final difference Fourier. The asymmetric unit, therefore, contains two crystallographically nonequivalent molecules of formula $Ru_2S_8C_{22}H_{40}N_4O_2BF_4$.

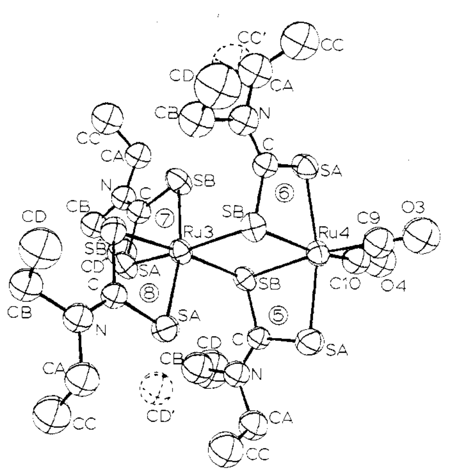

Figure 2. ORTEP drawing of the Ru3–Ru4 cation $[Ru_2(Et_2dtc)_4(CO)_2]^+$.

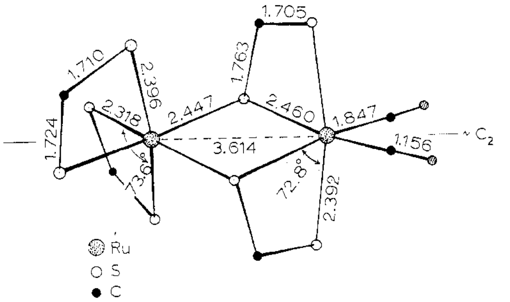

Figure 3. Drawing of the coordination core of $[Ru_2(Et_2dtc)_4(CO)_2]^+$ showing selected "averaged" distances and angles (see text).

The final atomic coordinates with their estimated standard deviations and the final thermal parameters are given in Table I. Tables of observed and calculated structure factors, general anisotropic temperature factor expressions, and weighted least-squares planes are available (supplemental material). Figures 1 and 2 present ORTEP perspectives of the molecular structures of the two nonequivalent cations and show the labeling scheme.

Results and Discussion

The asymmetric unit contains two crystallographically nonequivalent $[Ru_2(Et_2dtc)_4(CO)_2]BF_4$ molecules. The two

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(18) (a) The intensity data were processed as described in the "CAD4 and SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity I is given as

$$I = (K/\mathrm{NPI})(C - 2B)$$

where K = 20.1166 (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by

$$\sigma^2(I) = \left(\frac{K}{\mathrm{NPI}}\right)^2 [C + 4B + (pI)^2]$$

where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by

$$F_o = (I/Lp)^{1/2}$$

where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by

$$\sigma(F_o) = 1/2(\sigma(I)/I)F_o$$

(b) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described in the following reference. Frenz, B. A. In "Computing in Crystallography", Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds., Delft University Press, Delft, Holland, 1978, pp 64–71.

(19) The conventional primitive cell is $P\bar{1}$ (a = 16.757 Å, b = 17.451 Å, c = 14.198 Å, α = 95.79°, β = 114.10°, and γ = 87.80°) and the transformation which will convert the $A\bar{1}$ cell into this cell is

$$\begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 0.5 & 0.5 \end{pmatrix}$$

(20) Equivalent positions for this centric cell are x, y, z and $x, 1/2 + y, 1/2 + z$.

(21) The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as

$$R = (\sum ||F_o| - |F_c||)/\sum |F_o|$$

$$R_w = [(\sum w(|F_o| - |F_c|))^2/\sum w|F_o|^2]^{1/2}$$

The error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru1	0.19072 (5)	0.46436 (3)	0.05294 (5)	0.00352 (3)	0.00132 (1)	0.00333 (3)	−0.00082 (3)	−0.00047 (5)	0.00101 (3)
Ru2	0.23688 (4)	0.08912 (3)	0.52010 (4)	0.00275 (2)	0.00126 (1)	0.00302 (3)	−0.00062 (3)	−0.00002 (5)	0.00058 (3)
Ru3	0.30848 (4)	0.30952 (3)	0.45582 (4)	0.00299 (3)	0.00129 (1)	0.00268 (3)	−0.00097 (3)	−0.00042 (5)	0.00047 (3)
Ru4	0.37866 (4)	0.43231 (3)	0.43706 (5)	0.00284 (3)	0.00117 (1)	0.00366 (3)	−0.00060 (3)	−0.00008 (5)	0.00068 (3)
S1A	0.1348 (2)	0.01357 (11)	0.6799 (2)	0.00452 (11)	0.00205 (5)	0.00378 (10)	−0.00106 (12)	0.0012 (2)	0.0011 (1)
S1B	0.2811 (1)	0.02786 (9)	0.6059 (1)	0.00315 (8)	0.00148 (4)	0.00329 (9)	−0.00040 (10)	−0.0010 (2)	0.0007 (1)
S2A	0.2572 (1)	0.43397 (10)	0.9225 (1)	0.00395 (10)	0.00148 (4)	0.00359 (10)	0.00020 (11)	−0.0003 (2)	0.0004 (1)
S2B	0.1497 (1)	0.02509 (9)	0.4662 (1)	0.00281 (8)	0.00141 (4)	0.00346 (9)	−0.00055 (9)	−0.0004 (1)	0.0009 (1)
S3A	0.1275 (1)	0.13516 (10)	0.6014 (1)	0.00368 (9)	0.00167 (4)	0.00325 (9)	0.00008 (11)	0.0008 (2)	0.0011 (1)
S3B	0.1822 (1)	0.14600 (9)	0.4455 (1)	0.00363 (9)	0.00146 (4)	0.00350 (9)	−0.00048 (10)	0.0006 (2)	0.0014 (1)
S4A	0.3525 (1)	0.05675 (11)	0.4366 (2)	0.00316 (9)	0.00180 (5)	0.00427 (11)	−0.00090 (11)	0.0008 (2)	−0.0005 (1)
S4B	0.3306 (1)	0.14283 (10)	0.5680 (2)	0.00350 (9)	0.00155 (4)	0.00420 (10)	−0.00127 (10)	−0.0004 (2)	0.0000 (1)
S5A	0.2687 (2)	0.44145 (11)	0.3586 (2)	0.00370 (10)	0.00196 (5)	0.00401 (10)	−0.00063 (11)	−0.0007 (2)	0.0018 (1)
S5B	0.2707 (1)	0.40132 (9)	0.5062 (1)	0.00294 (8)	0.00139 (4)	0.00290 (9)	−0.00087 (9)	−0.0002 (1)	0.0001 (1)
S6A	0.4793 (1)	0.40243 (10)	0.5144 (2)	0.00304 (8)	0.00142 (4)	0.00410 (10)	−0.00069 (10)	−0.0010 (2)	0.0000 (1)
S6B	0.4127 (1)	0.33926 (9)	0.3792 (1)	0.00338 (9)	0.00135 (4)	0.00298 (9)	−0.00081 (10)	0.0004 (2)	0.0002 (1)
S7A	0.2168 (1)	0.28848 (10)	0.5454 (1)	0.00359 (9)	0.00207 (5)	0.00336 (9)	−0.00222 (10)	−0.0004 (2)	0.0010 (1)
S7B	0.3690 (1)	0.30977 (11)	0.5818 (1)	0.00351 (9)	0.00241 (5)	0.00322 (9)	−0.00229 (11)	−0.0010 (2)	0.0015 (1)
S8A	0.2386 (1)	0.29473 (10)	0.3350 (1)	0.00394 (9)	0.00125 (4)	0.00358 (9)	−0.00015 (10)	−0.0016 (2)	0.0001 (1)
S8B	0.3385 (1)	0.22315 (9)	0.3953 (1)	0.00377 (9)	0.00128 (4)	0.00386 (10)	−0.00066 (10)	−0.0012 (2)	0.0010 (1)
F1	0.1167 (7)	0.0418 (4)	−0.0035 (6)	0.0226 (9)	0.0037 (2)	0.0084 (5)	−0.0050 (7)	−0.0111 (10)	−0.0001 (5)
F2	0.0938 (6)	0.0821 (4)	0.1218 (6)	0.0104 (5)	0.0054 (3)	0.0131 (6)	0.0001 (7)	0.0081 (10)	−0.0012 (8)
F3	0.1877 (7)	0.1005 (4)	0.0420 (6)	0.0157 (7)	0.0038 (2)	0.0126 (6)	−0.0045 (7)	0.0009 (12)	0.0026 (6)
F4	0.1913 (7)	0.5282 (5)	0.5877 (7)	0.0091 (6)	0.0108 (4)	0.0170 (7)	0.0024 (8)	0.0036 (11)	0.0154 (8)
F5	0.2373 (5)	0.2447 (3)	0.9040 (4)	0.0102 (4)	0.0029 (2)	0.0068 (3)	−0.0019 (4)	−0.0038 (7)	0.0012 (4)
F6	0.1878 (4)	0.3240 (3)	0.9538 (6)	0.0049 (3)	0.0026 (1)	0.0189 (7)	0.0002 (4)	−0.0046 (8)	0.0052 (5)
F7	0.2232 (6)	0.2718 (3)	0.0367 (5)	0.0150 (6)	0.0045 (2)	0.0063 (3)	−0.0042 (6)	0.0030 (8)	0.0045 (4)
F8	0.3104 (4)	0.3048 (3)	0.9664 (4)	0.0045 (3)	0.0037 (2)	0.0085 (4)	−0.0015 (4)	−0.0017 (6)	0.0018 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O1	0.0529 (5)	0.4063 (3)	0.0087 (5)	7.7 (2)	C4A	0.5278 (7)	0.5663 (5)	−0.0561 (8)	7.1 (3)
O2	0.2619 (5)	0.3839 (3)	0.1393 (5)	7.2 (2)	C4B	0.5055 (7)	0.6448 (5)	0.0625 (8)	7.2 (3)
O3	0.4927 (5)	0.4733 (3)	0.3336 (5)	6.9 (2)	C4C	0.5453 (10)	0.5909 (7)	−0.1301 (10)	10.6 (5)
O4	0.3545 (5)	0.5393 (3)	0.5403 (5)	7.4 (2)	C4D	0.5198 (9)	0.6203 (6)	0.1389 (9)	9.1 (4)
N1	0.2331 (5)	0.0746 (3)	0.7605 (5)	5.0 (2)	C9	0.4488 (6)	0.4560 (4)	0.3721 (6)	5.2 (2)
N2	0.2071 (4)	0.4880 (3)	0.8114 (4)	4.1 (2)	C10	0.3607 (6)	0.4985 (4)	0.4997 (6)	5.1 (2)
N3	0.0497 (4)	0.1961 (3)	0.5163 (5)	4.5 (2)	C5	0.2144 (5)	0.4192 (3)	0.4294 (5)	3.4 (2)
N4	0.4723 (5)	0.1053 (3)	0.4996 (5)	5.7 (2)	C5A	0.0964 (6)	0.4373 (4)	0.3641 (6)	5.4 (2)
N5	0.1410 (4)	0.4173 (3)	0.4279 (5)	4.1 (2)	C5B	0.0964 (7)	0.3977 (5)	0.4914 (8)	6.9 (3)
N6	0.4638 (5)	0.1946 (3)	0.0440 (5)	4.8 (2)	C5C	0.0915 (7)	0.3935 (5)	0.2880 (8)	7.0 (3)
N7	0.2677 (5)	0.2921 (3)	0.6958 (5)	4.6 (2)	C6	0.4838 (5)	0.3434 (3)	0.4501 (5)	3.5 (2)
N8	0.2608 (4)	0.1948 (3)	0.2593 (4)	4.0 (2)	C6A	0.5947 (7)	0.3119 (5)	0.5209 (7)	6.6 (3)
C11	0.1073 (6)	0.4274 (4)	0.0252 (6)	5.3 (2)	C6B	0.4678 (7)	0.2495 (5)	0.0945 (7)	6.3 (3)
C12	0.2349 (6)	0.4145 (4)	0.1054 (6)	5.3 (2)	C6D	0.3980 (9)	0.2621 (6)	0.1550 (9)	9.4 (4)
C1	0.2167 (5)	0.0440 (4)	0.6937 (6)	4.1 (2)	C7	0.2830 (5)	0.2952 (4)	0.6192 (6)	4.0 (2)
C1A	0.1837 (7)	0.5821 (5)	0.3377 (7)	6.7 (3)	C7A	0.3272 (6)	0.3009 (4)	0.7576 (6)	5.2 (2)
C1B	0.3052 (7)	0.1011 (4)	0.7690 (7)	5.8 (3)	C7B	0.1890 (6)	0.2813 (4)	0.7241 (7)	5.6 (3)
C1C	0.1286 (9)	0.6312 (6)	0.3445 (10)	9.8 (4)	C7C	0.3758 (8)	0.2499 (5)	0.7551 (8)	7.4 (3)
C1D	0.3676 (8)	0.5661 (5)	0.3024 (8)	8.0 (3)	C7D	0.1383 (8)	0.3333 (5)	0.7535 (8)	7.3 (3)
C2	0.2068 (5)	0.4824 (4)	0.8878 (5)	3.7 (2)	C8	0.2768 (5)	0.2315 (3)	0.3197 (5)	3.4 (2)
C2A	0.2539 (6)	0.4499 (4)	0.7458 (6)	4.8 (2)	C8A	0.2097 (6)	0.2055 (4)	0.1944 (6)	5.1 (2)
C2B	0.1535 (7)	0.0283 (5)	0.2846 (7)	6.1 (3)	C8B	0.2910 (6)	0.1400 (4)	0.2555 (6)	4.8 (2)
C2C	0.3293 (7)	0.4718 (5)	0.7249 (8)	7.2 (3)	C8C	0.1252 (7)	0.2020 (5)	0.2205 (7)	6.7 (3)
C2D	0.0756 (8)	0.5058 (6)	0.7674 (9)	8.4 (4)	C8D	0.3720 (7)	0.1285 (5)	0.2083 (7)	6.9 (3)
C3	0.1096 (5)	0.1648 (3)	0.5209 (5)	3.5 (2)	C6C	0.6610 (14)	0.3331 (9)	0.5032 (14)	7.5 (6)[b]
C3A	−0.0156 (6)	0.7072 (4)	0.0802 (6)	5.2 (2)	C6C′	0.5756 (21)	0.3077 (14)	0.5884 (22)	10.2 (9)[b]
C3B	0.0370 (6)	0.2202 (4)	0.4433 (7)	5.7 (3)	C5D	0.0628 (14)	0.4340 (9)	0.5539 (14)	11.6 (6)[b]
C3C	−0.0055 (8)	0.7563 (6)	0.1391 (9)	8.4 (4)	C5D′	0.0523 (21)	0.3596 (14)	0.4679 (21)	7.3 (9)[b]
C3D	−0.0128 (8)	0.6871 (6)	−0.1175 (9)	8.7 (4)	B1	0.1427 (9)	0.5651 (6)	0.5588 (9)	6.9 (4)
C4	0.3967 (6)	0.6024 (4)	0.0003 (6)	4.4 (2)	B2	0.2392 (8)	0.2862 (6)	−0.0322 (8)	5.7 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. [b] Disordered atoms with the following refined multiplicities: 0.70, 0.63, 0.84, 0.51 for C6C, C6C′, C5D, C5D′, respectively.

cations, Ru1–Ru2 and Ru3–Ru4, have very similar geometries except for small but significant differences in distances and angles and large differences in the orientations of the ethyl groups. This can be seen in Figures 1 and 2 and by a comparison of the distances and angles within the $Ru_2S_8(CO)_2$ coordination cores (Table II). The entries in this table are separated into groups of chemically "equivalent" distances and angles assuming: (i) approximate C_2 symmetry for each cation (C_2 axis contains the Ru atoms) and (ii) the cations being chemically equivalent. In subsequent discussions, averaged values for the chemically equivalent distances and angles will be used and some of these are shown in Figure 3. Two of the terminal methyl carbon atoms (C6C and C5D) were found to be disordered between two positions. The disordered positions which refined to the smaller multiplicities (C6C′ and C5D′) are shown by dashed lines in Figure 2. No disorder was found in the Ru1–Ru2 cation. The cations are well separated in the unit cell. The shortest interionic contacts are between the fluorine atoms of the tetrafluoroborate anions and the carbonyl oxygen atoms and are 2.98 and 3.05 Å for F4⋯O4 and F6⋯O1, respectively.

The most important feature of the structure is the cis ar-

Table II. Selected Distances and Angles within the $Ru_2S_8(CO)_2$ Coordination Cores[a]

Distances, Å					
Ru1-Ru2	3.598 (1)	Ru1-S1A	2.391 (2)	Ru2-S3B	2.307 (2)
Ru3-Ru4	3.629 (1)	Ru1-S2A	2.393 (2)	Ru2-S4B	2.320 (2)
Ru1-C11	1.844 (9)	Ru4-S5A	2.389 (2)	Ru3-S7A	2.327 (2)
Ru1-C12	1.855 (9)	Ru4-S6A	2.393 (2)	Ru3-S8B	2.317 (2)
Ru4-C9	1.835 (9)	Ru2-S1B	2.463 (2)	S1A-S1B	2.881 (3)
Ru4-C10	1.852 (9)	Ru2-S2B	2.437 (2)	S2A-S2B	2.881 (3)
C11-O1	1.158 (9)	Ru3-S5B	2.433 (2)	S5A-S5B	2.876 (3)
C12-O2	1.154 (9)	Ru3-S6B	2.456 (2)	S6A-S6B	2.885 (2)
C9-O3	1.160 (9)	Ru2-S3A	2.396 (2)	S3A-S3B	2.822 (2)
C10-O4	1.151 (9)	Ru2-S4A	2.406 (2)	S4A-S4B	2.829 (3)
Ru1-S1B	2.462 (2)	Ru3-S7B	2.395 (2)	S7A-S7B	2.827 (3)
Ru1-S2B	2.449 (2)	Ru3-S8A	2.388 (2)	S8A-S8B	2.823 (2)
Ru4-S5B	2.454 (2)	S1B-S2B	3.333 (2)		
Ru4-S6B	2.474 (2)	S5B-S6B	3.303 (2)		
Angles, Deg					
C11-Ru1-C12	92.7 (4)	S2A-Ru1-S2B	73.02 (7)	Ru1-S1B-Ru2	93.88 (6)
C9-Ru4-C10	89.4 (4)	S1A-Ru1-S1B	72.82 (7)	Ru1-S2B-Ru2	94.86 (6)
S1B-Ru1-S2B	85.50 (6)	S5A-Ru4-S5B	72.83 (6)	Ru3-S5B-Ru4	95.87 (6)
S5B-Ru4-S6B	84.16 (6)	S6A-Ru4-S6B	72.67 (6)	Ru3-S6B-Ru4	94.79 (6)
S1B-Ru2-S2B	85.74 (6)	S3A-Ru2-S3B	73.73 (7)	Ru1-C11-O1	176.9 (8)
S5B-Ru3-S6B	84.99 (6)	S4A-Ru2-S4B	73.52 (7)	Ru1-C12-O2	178.8 (8)
		S7A-Ru3-S7B	73.54 (7)	Ru4-C9-O3	176.6 (8)
		S8A-Ru3-S8B	73.72 (7)	Ru4-C10-O4	175.3 (8)

[a] Numbers in parentheses are the estimated standard deviations of the last significant figure. The distances and angles are separated into groups which are chemically equivalent (see text).

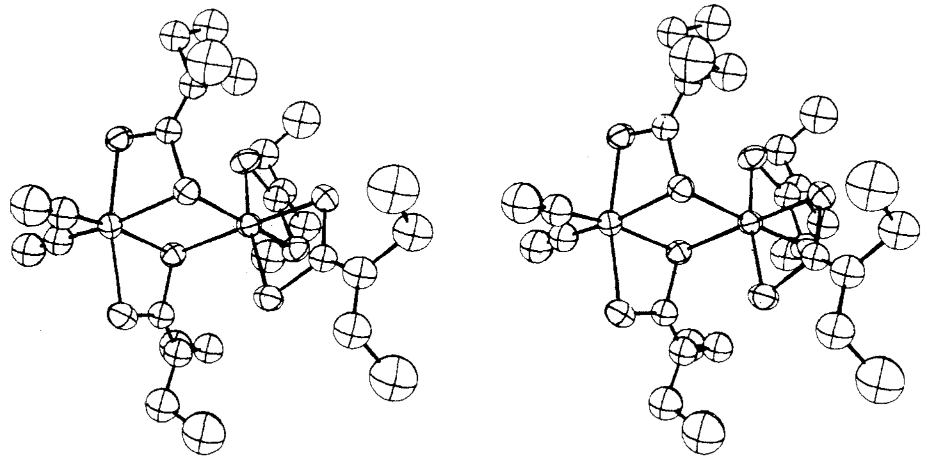

Figure 4. ORTEP stereoview of the Ru1-Ru2 cation.

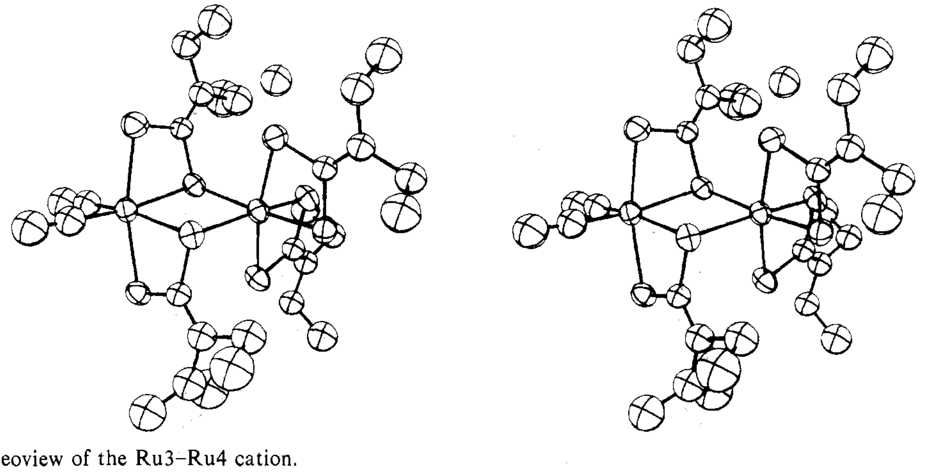

Figure 5. ORTEP stereoview of the Ru3-Ru4 cation.

rangement of the carbonyl ligands which are both coordinated to the same Ru atom. Since the compound was synthesized from **1** which has a trans carbonyl structure with one CO on each Ru atom, the oxidation reaction has resulted in a novel carbonyl rearrangement. The details of the rearrangement are complex and will be presented in a future publication.[17]

Each ruthenium atom is six-coordinate but appreciably distorted from ideal octahedral geometry. The overall stereochemistry of the cation is shown in the ORTEP stereoviews (Figures 4 and 5) and is best described as a bis chelated $Ru(dtc)_2$ moiety sharing two sulfur atoms of different dtc ligands of a six-coordinate $Ru(dtc)_2(CO)_2$ moiety. The two

Table III. Selected Distances and Angles within the Ligands and Anions

	ligand							
bond	1	2	5	6	3	4	7	8
				Distances, Å				
SA-C	1.700 (7)	1.701 (7)	1.712 (7)	1.707 (7)	1.712 (7)	1.704 (8)	1.719 (7)	1.714 (7)
SB-C	1.776 (7)	1.767 (7)	1.762 (7)	1.747 (7)	1.724 (7)	1.725 (8)	1.708 (7)	1.727 (7)
C-N	1.303 (9)	1.317 (8)	1.288 (8)	1.322 (9)	1.292 (8)	1.327 (9)	1.321 (9)	1.314 (8)
N-CA	1.50 (1)	1.500 (9)	1.50 (1)	1.52 (1)	1.50 (1)	1.50 (1)	1.49 (1)	1.487 (9)
N-CB	1.49 (1)	1.50 (1)	1.49 (1)	1.54 (1)	1.50 (1)	1.50 (1)	1.50 (1)	1.487 (9)
CA-CC	1.53 (2)	1.54 (1)	1.56 (1)	1.37 (2)[a]	1.50 (1)	1.54 (2)	1.52 (1)	1.54 (1)
CB-CD	1.56 (1)	1.54 (1)	1.35 (2)[a]	1.53 (1)	1.55 (1)	1.56 (2)	1.55 (1)	1.57 (1)
B1-F1	1.23 (1)	B1-F2	1.32 (1)	B1-F3	1.33 (1)	B1-F4	1.41 (2)	
B2-F5	1.38 (1)	B2-F6	1.35 (1)	B2-F7	1.31 (1)	B3-F8	1.38 (1)	
				Angles, Deg				
Ru-SA-C	89.3 (3)	88.8 (2)	89.3 (2)	88.6 (2)	86.5 (2)	86.2 (3)	88.6 (3)	87.0 (2)
Ru-SB-C	85.3 (3)[b]	85.5 (2)[b]	86.1 (2)[c]	85.1 (2)[c]	89.1 (2)	88.5 (3)	86.6 (3)	89.0 (2)
SA-C-SB	111.9 (4)	112.3 (4)	111.7 (4)	113.3 (4)	110.4 (4)	111.1 (4)	111.2 (4)	110.2 (4)
CA-N-CB	114.3 (7)	117.0 (6)	117.3 (7)	117.2 (7)	115.1 (6)	117.5 (7)	117.9 (6)	117.2 (6)

[a] Distances involve a disordered C atom and are reported only for the atoms of higher multiplicity. [b] Distance for Ru1. [c] Distance for Ru4.

ruthenium atoms of each cation have coordination core geometries of opposite chiralities [Figure 4 shows Ru1, Λ configuration, and Ru2, Δ configuration, while Figure 5 shows Ru3, Λ configuration, and Ru4, Δ configuration]. Similar opposite chirality metal centers have also been found for the complexes $[Co_2(Et_2dtc)_5]^+$,[3] $[Rh_2(Me_2dtc)_5]^+$,[4] and α-$[Ru_2(i\text{-}Pr_2dtc)_5]^{+}$[2] which have the same basic coordination stereochemistry as **2** except that one dtc ligand has been replaced by two carbonyl ligands. Of these, only α-$[Ru_2(i\text{-}Pr_2dtc)_5]^+$ has a metal–metal bond (Ru–Ru, 2.789 (4) Å)[2] while the others show no significant metal–metal interaction [Co–Co = 3.372 (5) Å;[3] Rh–Rh = 3.556 (1) Å;[4] and in **2**, Ru–Ru = 3.614 (1) Å]. The Ru–Ru distance in the mixed-valence Ru(II)–Ru(III) compound **2** is slightly shorter than in the Ru(II)–Ru(II) dicarbonyl starting compound **1**, the latter being 3.654 (2) Å.[7] In α-$[Ru_2(i\text{-}Pr_2dtc)_5]^+$, the short Ru–Ru distance is caused by bond formation and spin pairing between the two Ru(III) low-spin d^5 centers whereas the stable spin-paired d^6 electronic configurations of each metal in the Co(III)–Co(III), Rh(III)–Rh(III), and Ru(II)–Ru(II) complexes results in no metal–metal bonding. It might be expected that the mixed-valence compound **2** should show some metal–metal bonding; however, the long Ru–Ru distance argues against this.

The Ru–S(bridging) distances (average 2.454 (2) Å) are longer than the Ru–S(nonbridging) distances (average 2.369 (2) Å). This is a consequence of the increased coordination of the bridging sulfur atoms and has also been observed in all other similar bridged dtc complexes which do *not* have significant metal–metal bonding.[3,4,7] In these compounds the M–S(bridging) distances also show a significant asymmetry such that the M–S(bridging) bonds within the four-membered dtc chelate rings are shorter than the ones spanning the bis- and tris-chelated moieties. This is clearly not the case with **2** as shown in Figure 3. The Ru–S(bridging) distances which are not within the dtc chelate rings are actually slightly shorter (2.447 (2) vs. 2.460 (2) Å). This undoubtedly is caused by the trans influence of the carbonyl groups which are trans to the Ru–S(bridging) bonds within the dtc chelate rings. A similar lengthening of the Ru–S bonds trans to the CO ligands is observed in **1**. The average Ru–S(bridging) distance in **2** is slightly shorter than in **1** (2.454 (2) vs. 2.478 (3) Å). This same trend is observed in the nonbridging Ru–S distances (average values in **1** and **2** are 2.397 (4)[7] and 2.369 (2) Å, respectively) and results from the expected Ru–S bond shortening upon increasing the metal oxidation state. The $Ru_2S(bridging)_2$ ring in **2** is approximately planar. The distances of the following atoms from their weighted least-squares planes in each cation are (for the Ru1–Ru2 cation) Ru1 = −0.003 (1) Å, Ru2 = −0.002 (1) Å, S1B = 0.022 (2) Å, and S2B = 0.021 (2) Å and (for the Ru3–Ru4 cation) Ru3 = −0.006 (1) Å, Ru4 = −0.007 (1) Å, S6B = 0.063 (2) Å, and S7B = 0.061 (2) Å.

The Ru–CO distances [average value of 1.847 (9) Å] are within the range normally observed in ruthenium carbonyl complexes.[7] The Ru–CO distances in **1** are 1.75 (1) and 1.82 (1) Å and therefore are considerably shorter than in **2**. This is consistent with increased π back-bonding due to the greater electron density on the ruthenium atoms in **1**. The infrared CO stretching frequencies are also in agreement with this [**1**, ν(CO) = 1925 cm^{-1}; **2**, ν(CO) = 2055 and 1998 cm^{-1}]. The C–O distances in **2** [average value of 1.156 (9) Å] are also normal.

Distances and angles within the ligands and the BF_4 anions are presented in Table II. The bond lengths within the nonbridging Et_2dtc ligands (ligands 3, 4, 7, and 8) are not unusual with mean C–S and S_2C–N distances of 1.717 (7) and 1.314 (8) Å, respectively, both being indicative of the expected partial double bond character. However, in the bridging Et_2dtc ligands (ligands 1, 2, 5, and 6), the C–S bond lengths in each ligand show a marked asymmetry. The average C–S(bridging) bond length (1.763 (7) Å is significantly longer (ca. 8σ) than the average C–S(nonbridging) bond length 1.705 (7) Å. This is ascribed to nonparticipation of the bridging-sulfur p_π electrons in the normal conjugation associated with the $S_2C\overset{\cdots}{-}NR_2$ system, because of its involvement in the Ru–S σ bonding. A similar asymmetry has been noted in other dtc-bridged bimetallic complexes.[1-4,7] Other distances and angles in the bridging Et_2dtc ligands are normal.

An obvious question in this mixed-valence complex is the assignment of oxidation state. For example, is the complex best described as $Ru^{III}(Et_2dtc)_2^+$ and $Ru^{II}(Et_2dtc)_2(CO)_2$ moieties with isolated oxidation states or as an intermediate oxidation state compound with delocalization of the unpaired electron. From the crystallographic data alone this question is difficult if not impossible to answer; however, the nearly identical lengths of the Ru–S bonds which do not involve bridging S atoms and which are not trans to bridging S atoms and the significant shortening of the Ru–CO distances in **1** compared with those in **2** suggests that **2** is best described as an intermediate oxidation state compound. Unfortunetly, these bond length arguments are somewhat risky since the above comparisons involve ruthenium coordination cores which have different compositions (in **1**, RuS_5C; in **2**, RuS_6 and RuS_4C_2). Spectroscopic data also suggest that **2** is not simply a composite of a Ru(III) and a Ru(II) species. For example, the UV–vis spectrum of **2** is quite different from a simple sum of spectra of $Ru(Et_2dtc)_3$ and *cis*-$Ru(Et_2dtc)_2(CO)_2$. Additionally, the ^1H 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.

Acknowledgment. This research was supported by the National Science Foundation (NSF Grant No. CHE-7821840). We also thank NSF for partial support of our X-ray diffraction and structure solving equipment (NSF Grant No. CHE-7728505) and Engelhard Industries for a generous loan of $RuCl_3$.

Registry No. 1, 58320-56-2; **2**·BF_4, 72867-99-3.

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.

Contribution from the Departments of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, and Rutgers, The State University of New Jersey, Newark, New Jersey 07102

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

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Received September 14, 1979

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)°, $\gamma = 113.37(4)$°, $d_{calcd} = 1.807$ g/cm^3, and $d_{obsd} = 1.808$ (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 $Cu^{II}(2,3,2\text{-tet})(ClO_4)_2$ monomers with characteristic N_4O_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 $Cu(3,3,3\text{-tet})(ClO_4)_2$ 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 $Cu(2,3,2\text{-tet})^{2+}$ complex in detail. We report here the crystal structure of $Cu(2,3,2\text{-tet})(ClO_4)_2$ along with a comparison of its structural features with those reported for other Cu(II)–polyamine species. Preliminary structural features of the $Cu(3,3,3\text{-tet})(ClO_4)_2$ complex are also described and used to help explain the large difference in formation constants between the $Cu(2,3,2\text{-tet})^{2+}$ and $Cu(3,3,3\text{-tet})^{2+}$ complexes.

Experimental Section

1. Preparation of $Cu(2,3,2\text{-tet})(ClO_4)_2$. 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·$2H_2O$ was obtained.

After 2 days, dark purple prisms of the title complex crystallized from a chilled (~−10 °C) mixture of 80 mL of CH_3OH, 20 mL of H_2O, 0.75 g of $Cu(ClO_4)_2 \cdot 6H_2O$ (2.0 mmol), and 0.39 g of 2,3,2-tet·$2H_2O$ (2.0 mmol). The product was collected by filtration, washed with 5 mL of 95/5 (v/v) CH_3OH/H_2O, 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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[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.

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[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.

0020-1669/80/1319-0940$01.00/0