Table IX. Important Planes[a] and Atomic Deviations Therefrom (Å), for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

(A) C(11)-C(12)-C(16)-C(17) Plane

$$-0.6827X - 0.2654Y - 0.6808Z + 2.0278 = 0$$

dev: C(11),[b] 0.025 (7); C(12),[b] −0.039 (7); C(16),[b] 0.040 (7); C(17),[b] −0.026 (7); Ta, −1.5003 (2); C(13), 1.121 (9); C(15), 1.307 (10); C(14), 2.100 (10)

(B) C(11)-Ta-C(17) Plane (Exact)

$$-0.8545X + 0.5027Y - 0.1312Z + 0.7301 = 0$$

dev: C(12), −1.245 (7); C(16), −1.192 (7)

(C) Cl(1)-Ta-Cl(2) Plane (Exact)

$$0.1658X - 0.7981Y - 0.5793Z + 2.9509 = 0$$

(D) Cyclopentadienyl Plane (C(1) → C(5))

$$0.6658Z - 0.7234Y - 0.1827Z + 2.9879 = 0$$

dev: C(1),[b] 0.002 (6); C(2),[b] 0.003 (6); C(3),[b] −0.006 (6); C(4),[b] 0.007 (6); C(5),[b] −0.005 (6); Ta, +2.0939 (2); C(6), −0.136 (8); C(7), −0.113 (9); C(8), −0.157 (8); C(9), −0.050 (9); C(10), −0.145 (9); C(11), 2.852 (6); C(17), 2.824 (7); H(6A), −0.90 (7); H(6B), 0.16 (10); H(6C), 0.34 (8); H(7A), −0.92 (8); H(7B), 0.34 (8); H(7C), 0.16 (8); H(8A), −0.93 (8); H(8B), 0.27 (10); H(8C), 0.01 (10); H(9A), −0.86 (8); H(9B), 0.28 (12); H(9C), 0.20 (11); H(10A), −0.98 (8); H(10B), 0.24 (12); H(10C), 0.01 (10)

Interplanar Angles (Deg) for Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2

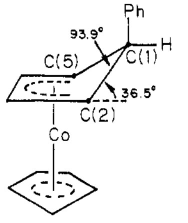
A/B	122.64	B/C	117.83
A/D	97.95	B/D	155.31
C/D	142.52		

[a] Orthonormal coordinates. [b] These atoms used in defining the plane.

(ii) The tantalum–carbon σ bonds are much longer than any other bonds around the metallacyclopentane ring. Values are 2.217 (8) Å for the $-C_4H_8-$ complex and 2.196 [6] Å for the $-C_7H_{12}-$ complex.

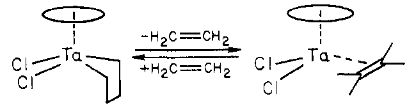
(iii) The molecules contain very acute C(α)–Ta–C(α') angles (72.45 (28)° in the $-C_4H_8-$ complex and 71.47 (25)° in the $-C_7H_{12}-$ complex). These may, however, result simply as a geometric requirement of item ii.

It is interesting to note that a number of metal complexes of cyclopenta*diene* ligands have an "opened-envelope" conformation, along with abnormally small (substantially less than 109.28°) internal angles at C(1). Thus, Co(η^5-C_5H_5)(η^4-C_5H_5Ph) (III) has an internal angle of 93.9 (15)° at C(1) and has a bend of 36.5° across the C(2)···C(5) vector.[17,18]



II

A final thought is that the orientation of the metallacyclopentane ligand may, in some way, facilitate the observed[6] reversible loss of olefin from this class of Complexes (see eq 4). Possibly, some direct Ta···C(β) interaction is more easily attainable in this geometry.



III IV (4)

We have determined that the resultant olefin complex (IV in eq 4) has a solid-state geometry in which the olefinic C–C vector lies parallel to the Cl···Cl vector.[19] The acetylene complex Ta(η^5-C_5Me_5)(η^2-PhC≡CPh)Cl_2 has a similar arrangement;[20] but the benzyne complex Ta(η^5-C_5Me_5)(η^2-C_6H_4)Me_2 has the benzyne ligand lying perpendicular to the C(Me)···C(Me) vector.[12,21]

Acknowledgment. We thank Professor R. R. Schrock for providing the samples. This work was supported by the National Science Foundation (Grant CHE77-04981, to M.R.C.).

Registry No. Ta(η^5-C_5Me_5)(C_4H_8)Cl_2, 71936-69-1; Ta(η^5-C_5Me_5)(C_7H_{12})Cl_2, 71936-59-9.

Supplementary Material Available: A table of data-processing formulas and listings of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the Hydrogen-Bonded Dimer of ((Phenylazo)acetaldoximato-*N*,*N'*)((phenylazo)acetaldoxime-*N*,*N'*)copper(I)

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The product of the reaction of (phenylazo)acetaldoxime, $C_6H_5N{=}C(CH_3){=}NOH$ (LH), with copper(II) acetate has been shown by a crystal structure analysis to be a copper(I) complex, Cu(L)(LH), which is associated into dimers through short O–H–O hydrogen-bonding interactions. Crystals of this material are monoclinic, space group $C2/c$, with a = 9.727 (3) Å, b = 21.824 (7) Å, c = 16.948 (5) Å, and β = 106.66 (2)°. Least-squares refinement, based on 2723 nonzero data, converged to a conventional R factor of 0.063. Evidence for formulation as a copper(I) complex includes the distorted tetrahedral geometry about the metal ion and a pair of short O···O intermolecular contacts of 2.425 (5) Å, indicative of strong hydrogen bonding between monomers. The resulting dimer has crystallographic twofold symmetry and virtual D_2-222 symmetry. The ligands are nearly planar, with a mean Cu–N distance of 1.992 (6) Å. The observed structure and the copper(I) formulation are consistent with other physical and chemical properties of this compound.

Introduction

A series of compounds derived from arylazo oximes, LH = ArN=NC(R)=NOH, and copper(II) acetate have been reported by Chakravorty et al.[1] These compounds were formulated as copper(II) bis chelates of the deprotonated oximes. Surprisingly, all were found to be diamagnetic. A

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Table I. Crystal Data and Experimental Parameters

A. Crystal Data

formula	$Cu_2C_{32}H_{34}N_{12}O_4$	Vol	3446 (2) $Å^3$
fw	777.79	*Z*	4
a	9.727 (3) Å	density (obsd)	1.49 (2) g cm^{-3}
b	21.824 (7) Å	density (calcd)	1.50 g cm^{-3}
c	16.948 (5) Å	space group	*C*2/*c*
β	106.66 (2)°	μ(Mo Kα)	13.4 cm^{-1}

B. Experimental Parameters

radiation	Mo Kα $\bar{\lambda}$(Kα) = 0.710 73 Å, graphite monochromator	scan range	−1.1° from Kα_1 to +1.2° from Kα_2
temp	23 °C	bkgd counting	stationary counts for half of scan time at each end of scan
receiving aperture	circular, 4-mm diam, 20 cm from crystal		
scan rate	variable, 2–12° min^{-1}	2θ(max)	55°
		data collected	4003
		data with $F_o^2 > 3\sigma(F_o^2)$	2723

molecular weight determination showed that a representative member of the series was dimeric in benzene; consequently, a bridged structure of the copper(II) acetate type[2] was considered a possibility. Some degree of magnetic coupling is commonly found in copper(II) complexes of this structure,[3-5] and plausible bidentate bridging configurations of the azo oxime ligand could be evisioned.[1] At least one copper(II) complex with the copper(II) acetate structure, $Cu_2(dpt)_4$ (dpt = 1,3-diphenyltriazenido), is diamagnetic at room temperature.[6,7] Subsequent work suggested another possible structure in which the two metal atoms were linked by a pair of bidentate N,O-bridging oximato ligands to form a planar $Cu(NO)_2Cu$ ring. This type of structure has recently been found for several oximato complexes of copper(II) which show strong magnetic coupling,[8-10] including some which are diamagnetic at room temperature.[8,9]

Our crystal structure analysis of one member of this series (Ar = C_6H_5, R = CH_3), carried out in order to determine the structural basis for its diamagnetism, has unexpectedly shown it to be a complex of copper(I), with one of the two ligands present in its protonated form.

Experimental Section

Collection and Reduction of X-ray Data. Crystals of the title compound were supplied by Professor A. Chakravorty. A crystal of irregular shape with approximate dimensions 0.5 × 0.5 × 0.3 mm was selected and mounted on a glass fiber. Initial centering of reflections, generation of unit cell vectors, and assignment of indices were performed on a Syntex P2$_1$ diffractometer by methods described elsewhere.[11] Monoclinic symmetry was suggested by the interaxial angles and confirmed by axial rotation photographs. Refined cell parameters were obtained as previously described.[12] Density was measured by flotation in a carbon tetrachloride–heptane mixture. Crystal data are summarized in part A of Table I. Intensity data were collected by the 2θ–θ scan technique in bisecting geometry. Experimental parameters are given in part B of Table I. Three standard reflections were monitored after each 50 data; no significant change was observed in their intensities. The data showed systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) consistent with space groups *Cc* and *C*2/*c*. Six reflections were strong enough to exceed the valid range of the coincidence correction. These were remeasured at a lower filament current and adjusted accordingly during the processing. Data processing was accomplished by previously described methods.[12] The *p* factor in the expression[13] for the standard deviations of the observed intensities was set at 0.05. No correction was made for absorption.

Table II. Atomic Positional and Isotropic Thermal Parameters

atom	*x*	*y*	*z*	*B*, $Å^2$
Cu	0.06743 (7)[a]	0.12503 (3)	0.38480 (4)	*b*
O(1)	−0.2018 (4)	0.0707 (2)	0.2650 (2)	
O(2)	0.2169 (5)	0.1769 (2)	0.2649 (2)	
N(1)	−0.0799 (5)	0.0647 (2)	0.3269 (3)	
N(2)	0.0787 (5)	−0.0017 (2)	0.4141 (3)	
N(3)	0.1505 (5)	0.0473 (2)	0.4406 (2)	
N(4)	0.1560 (5)	0.1856 (2)	0.3266 (2)	
N(5)	0.0853 (5)	0.2518 (2)	0.4144 (3)	
N(6)	0.0402 (5)	0.2028 (2)	0.4405 (2)	
C(1)	−0.0468 (6)	0.0081 (2)	0.3507 (3)	
C(2)	−0.1370 (6)	−0.0464 (3)	0.3137 (4)	
C(3)	0.2760 (6)	0.0377 (2)	0.5060 (3)	3.03 (9)
C(4)	0.3585 (6)	0.0895 (3)	0.5366 (4)	3.79 (10)
C(5)	0.4851 (8)	0.0843 (3)	0.6002 (4)	4.87 (13)
C(6)	0.5273 (8)	0.0265 (4)	0.6333 (5)	5.25 (14)
C(7)	0.4463 (8)	−0.0257 (4)	0.6039 (5)	5.59 (16)
C(8)	0.3213 (7)	−0.0195 (3)	0.5399 (4)	4.55 (12)
C(9)	0.1469 (6)	0.2419 (2)	0.3501 (3)	
C(10)	0.2005 (7)	0.2962 (2)	0.3141 (4)	
C(11)	−0.0204 (6)	0.2126 (2)	0.5056 (3)	3.01 (9)
C(12)	−0.0717 (6)	0.1612 (3)	0.5361 (4)	3.72 (10)
C(13)	−0.1341 (8)	0.1670 (3)	0.6012 (4)	4.74 (13)
C(14)	−0.1435 (8)	0.2240 (3)	0.6335 (4)	5.01 (14)
C(15)	−0.0926 (8)	0.2750 (4)	0.6045 (4)	5.06 (14)
C(16)	−0.0314 (7)	0.2694 (3)	0.5399 (4)	4.27 (12)
H(4)[c]	0.3274	0.1292	0.5128	3.7[d]
H(5)	0.5424	0.1205	0.6209	4.8
H(6)	0.6152	0.0228	0.6774	5.3
H(7)	0.4750	−0.0651	0.6285	5.7
H(8)	0.2653	−0.0554	0.5176	4.5
H(12)	−0.0653	0.1215	0.5124	3.7
H(13)	−0.1691	0.1312	0.6225	4.7
H(14)	−0.1886	0.2279	0.6768	5.0
H(15)	−0.0960	0.3142	0.6297	5.1
H(16)	0.0024	0.3055	0.5181	4.3

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] Atoms for which no *B* value is listed were refined anisotropically; thermal parameters for these atoms are given in Table II. [c] Hydrogen atoms are numbered corresponding to the carbon atoms to which they are bound. [d] Each hydrogen atom was assigned a thermal parameter equal to that of the corresponding carbon atom.

Structure Solution and Refinement. Intensity statistics favored the centrosymmetric space group *C*2/*c* (No. 15, second setting). The position of the single copper atom in the asymmetric unit was determined from a Patterson synthesis.[14] Subsequent difference Fourier syntheses revealed all other nonhydrogen atoms. Anisotropic thermal parameters were introduced for all nonhydrogen atoms except the phenyl carbons. At convergence of least-squares refinement of all nonhydrogen atoms, the conventional *R* factors were $R_1 = 0.066$ and $R_2 = 0.090$. A difference map at this point showed no residuals greater than 0.2 e/$Å^3$. No compelling evidence for the methyl hydrogen atoms was found on this map. In the final refinement, all phenyl hydrogen atoms were included at fixed idealized positions (C–H = 0.95 Å,

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Table III. Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	4.23 (3)	1.67 (2)	3.38 (3)	−0.55 (2)	1.42 (2)	0.02 (2)
O(1)	3.92 (18)	2.97 (16)	4.01 (17)	−0.50 (14)	0.10 (14)	0.50 (14)
O(2)	5.48 (21)	3.11 (17)	3.76 (16)	−0.72 (15)	2.92 (16)	−0.67 (14)
N(1)	3.32 (19)	2.46 (17)	2.99 (17)	−0.44 (14)	0.90 (14)	0.26 (13)
N(2)	3.76 (21)	2.06 (17)	3.66 (18)	−0.39 (14)	0.73 (16)	0.32 (14)
N(3)	3.52 (19)	2.02 (15)	2.86 (16)	−0.46 (14)	1.06 (14)	−0.02 (13)
N(4)	4.07 (20)	2.39 (17)	2.88 (17)	−0.64 (15)	1.76 (15)	−0.35 (13)
N(5)	4.91 (23)	1.96 (17)	3.42 (18)	−0.37 (15)	2.07 (17)	−0.12 (14)
N(6)	3.61 (19)	1.96 (15)	2.70 (16)	−0.47 (13)	1.38 (14)	0.03 (12)
C(1)	3.86 (25)	2.21 (20)	3.35 (22)	−0.34 (17)	1.00 (18)	0.12 (16)
C(2)	4.44 (27)	2.31 (20)	5.00 (29)	−0.93 (19)	−0.48 (22)	0.10 (20)
C(9)	4.54 (26)	1.99 (19)	3.15 (21)	−0.46 (17)	1.77 (19)	−0.31 (16)
C(10)	7.23 (37)	2.13 (20)	4.86 (28)	−0.94 (21)	3.77 (28)	−0.09 (19)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Bond Distances (Å)

	(a) Copper Coordination Sphere		
Cu-N(1)	1.985 (4)	Cu-N(4)	1.988 (4)
Cu-N(3)	1.997 (4)	Cu-N(6)	1.996 (4)
	(b) Azo Oxime Ligands		
N(1)-O(1)	1.346 (6)	N(4)-O(2)	1.347 (5)
N(1)-C(1)	1.311 (6)	N(4)-C(9)	1.302 (6)
C(1)-C(2)	1.503 (7)	C(9)-C(10)	1.493 (7)
C(1)-N(2)	1.393 (7)	C(9)-N(5)	1.403 (6)
N(2)-N(3)	1.285 (6)	N(5)-N(6)	1.284 (6)
N(3)-C(3)	1.409 (7)	N(6)-C(11)	1.408 (6)
O(1)-O(2)′[a]	2.425 (5)		
	(c) Phenyl Rings		
C(3)-C(4)	1.398 (8)	C(11)-C(12)	1.388 (8)
C(4)-C(5)	1.388 (9)	C(12)-C(13)	1.409 (8)
C(5)-C(6)	1.395 (10)	C(13)-C(14)	1.372 (10)
C(6)-C(7)	1.394 (10)	C(14)-C(15)	1.365 (10)
C(7)-C(8)	1.385 (9)	C(15)-C(16)	1.394 (9)
C(8)-C(3)	1.392 (8)	C(16)-C(11)	1.386 (8)
	mean C-C (phenyl) = 1.389 (12)[b]		

[a] The prime denotes an atom related to its counterpart in the asymmetric unit by a twofold axis. [b] The number in parentheses after a mean distance or angle is the standard deviation of an individual measurement as estimated by the variation in values of presumably equivalent lengths.

Table V. Bond Angles (Deg)

	(a) Copper Coordination Sphere		
N(1)-Cu-N(3)	78.9 (2)	N(4)-Cu-N(6)	78.7 (2)
N(1)-Cu-N(4)	123.3 (2)	N(3)-Cu-N(6)	126.1 (2)
N(1)-Cu-N(6)	128.5 (2)	N(3)-Cu-N(4)	128.8 (2)
	(b) Azo Oxime Ligand		
Cu-N(1)-O(1)	132.1 (3)	Cu-N(4)-O(2)	132.0 (3)
Cu-N(1)-C(1)	113.2 (4)	Cu-N(4)-C(9)	113.5 (3)
O(1)-N(1)-C(1)	114.5 (4)	O(2)-N(4)-C(9)	114.4 (4)
N(1)-C(1)-C(2)	123.7 (5)	N(4)-C(9)-C(10)	124.2 (4)
N(1)-C(1)-N(2)	117.7 (5)	N(4)-C(9)-N(5)	117.7 (4)
C(2)-C(1)-N(2)	118.5 (5)	C(10)-C(9)-N(5)	118.1 (4)
C(1)-N(2)-N(3)	114.2 (4)	C(9)-N(5)-N(6)	113.8 (4)
N(2)-N(3)-C(3)	114.3 (4)	N(5)-N(6)-C(11)	113.9 (4)
Cu-N(3)-C(3)	129.8 (3)	Cu-N(6)-C(11)	129.9 (3)
Cu-N(3)-N(2)	115.8 (3)	Cu-N(6)-N(5)	116.2 (3)
N(1)-O(1)-O(2)′	104.2 (3)	N(4)-O(2)-O(1)′	104.1 (2)
	(c) Phenyl Rings		
N(3)-C(3)-C(4)	116.6 (5)	N(6)-C(11)-C(12)	116.5 (5)
N(3)-C(3)-C(8)	123.9 (5)	N(6)-C(11)-C(16)	124.3 (5)
C(4)-C(3)-C(8)	119.5 (5)	C(12)-C(11)-C(16)	119.2 (5)
C(3)-C(4)-C(5)	120.6 (6)	C(11)-C(12)-C(13)	120.0 (6)
C(4)-C(5)-C(6)	118.7 (7)	C(12)-C(13)-C(14)	119.2 (6)
C(5)-C(6)-C(7)	121.7 (7)	C(13)-C(14)-C(15)	121.5 (7)
C(6)-C(7)-C(8)	118.6 (7)	C(14)-C(15)-C(16)	119.5 (7)
C(7)-C(8)-C(3)	121.0 (7)	C(15)-C(16)-C(11)	120.7 (6)
	mean C-C-C (phenyl) = 120.0 (11)		

trigonal geometry). This refinement converged to discrepancy factors 0.063 and 0.085.

Table VI. Least-Squares Planes

Planes and Deviations[a]

(1) $0.7220X - 0.1213Y - 0.6811Z^b = -5.4761$			
Cu	0.013	C(1)	0.017
N(1)	−0.019	C(2)*	0.066
N(2)	0.000	O(1)*	0.011
N(3)	−0.010		
(2) $-0.7256X + 0.1205Y - 0.6775Z = -3.0341$			
Cu	0.012	C(9)	0.017
N(4)	−0.019	C(10)*	0.050
N(5)	−0.002	O(2)*	−0.004
N(6)	−0.008		
(3) $0.7349X - 0.1346Y - 0.6674Z = -5.4051$			
C(3)	−0.001	C(6)	−0.001
C(4)	−0.003	C(7)	−0.004
C(5)	0.004	C(8)	0.004
(4) $-0.7378X + 0.1352Y - 0.6613Z = -2.8424$			
C(11)	0.001	C(14)	0.004
C(12)	−0.001	C(15)	−0.004
C(13)	−0.001	C(16)	0.002

Angles between Normals to Planes

planes	angle, deg	planes	angle, deg
1-2	94.4	2-4	1.4
1-3	1.4		

[a] Tabulated values are distances in Å to the plane. Atoms marked with an asterisk were not used in the definition of the plane, while all others were given unit weights. [b] Equations of planes are expressed with respect to coordinates (*X*, *Y*, *Z*) referred to an orthogonal system (*A*, *B*, *C*) with *A* parallel to *a*, *B* parallel to *C** × *a*, and *C* parallel to *A* × *B*.

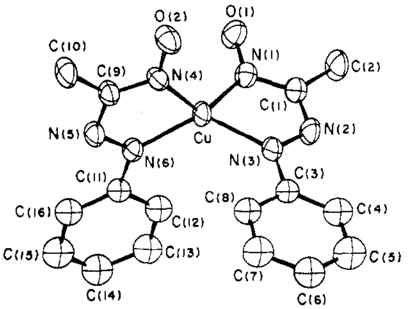

Figure 1. A view of the molecular structure of one monomer. Thermal ellipsoids are drawn at the 50% probability level.

In all structure factor calculations, atomic scattering factors, including anomalous terms for Cu, were taken from ref 15. The final standard deviation of an observation of unit weight was 2.47. The

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

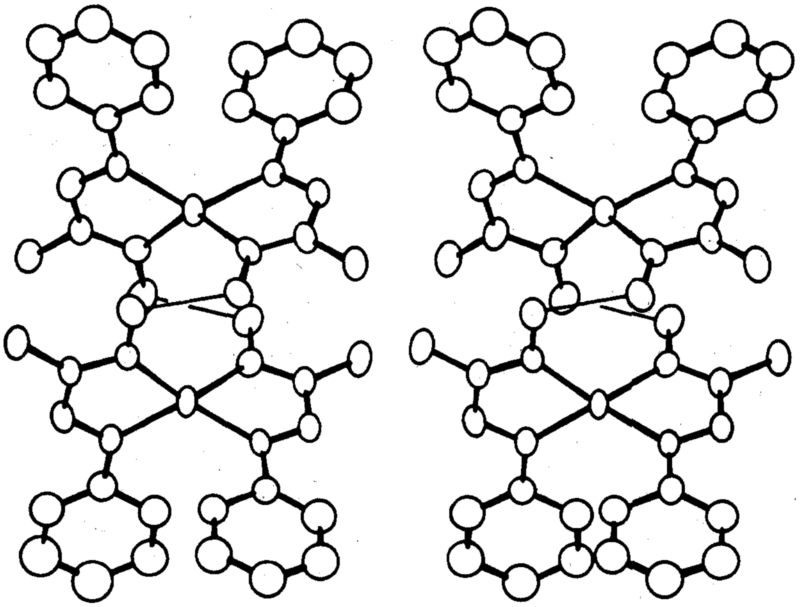

Figure 2. A stereoscopic view of the hydrogen-bonded dimer. Hydrogen-bonding interactions are denoted by light lines between the oxygen atoms involved.

function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Calculation of structure factors for the 1275 data with $F_o^2 \leq 3\sigma(F_o^2)$ showed 19 reflections with $\Delta F/\sigma \geq 3$; of these, 5 had $\Delta F/\sigma > 5$.

Final atomic positional and isotropic thermal parameters are tabulated in Table II; anisotropic thermal parameters are listed in Table III. Tables IV and V contain bond distances and angles, respectively. Data on least-squares planes are given in Table VI. A table of observed and calculated structure factors is available as supplementary material.

Description of the Structure and Discussion

The principal result of this crystal structure analysis is the demonstration that the title compound is in fact a copper(I) complex in which one chelating ligand is present as a neutral oxime, while the other exists in the deprotonated oximato form. The Cu(LH)(L) units are linked into dimers by a pair of short O–H–O hydrogen bonds. A view of the structure of one monomer unit is shown in Figure 1, while Figure 2 is a stereoscopic view of the dimer. The structural evidence for the Cu(I) formulation includes the distorted tetrahedral configuration about the copper atom and the short O···O contacts of 2.425 (5) Å between the halves of the dimer. The observed O···O separation is substantially shorter than twice the oxygen van der Waals radius[16] and near the short end of the range of distances expected for a pair of oxygen atoms linked by a hydrogen bond.[17] The presence of such a hydrogen bond dictates the Cu(LH)(L) stoichiometry, consistent with the presence of Cu(I).

No evidence for the oxime hydrogen atom appeared on a difference Fourier map calculated after refinement of all nonhydrogen atoms. A final partial difference map, based upon data with $(\sin\theta)/\lambda \leq 0.30$, did show a peak in a reasonable position between the two oxygen atoms (O–H distances of 1.15 and 1.31 Å, O–H–O angle of 160°). No attempt was made to refine a hydrogen atom at the position of this peak, and we do not consider the results of the partial difference Fourier synthesis to be firm evidence for asymmetric placement of the bridging hydrogen atom. A neutron diffraction study would be required to establish this point.

The formation of a discrete dimeric transition-metal complex by hydrogen-bonding interactions is unusual but not unprecedented. An early example of such a system was the mixed cobalt-nickel dimer $[CoNi(Eta)_3(EtaH)_3]^{2+}$ (where EtaH = 2-aminoethanol) in which two octahedral tris-chelate complexes are joined face-to-face by three O–H–O hydrogen bonds.[18] Closely related dicobalt and dinickel complexes have subsequently been reported.[19] The O···O hydrogen-bonding distances in these systems range from 2.40 to 2.7 Å. A series of copper(II) complexes of general formula $[Cu_2(tren)_2X_2]^{2+}$ (tren = 2,2′,2″-triaminotriethylamine; X = CN^-, Cl^-, NCO^-, NCS^-) has also been reported.[20,21] These dimers are formed by relatively long X–H–N hydrogen-bonding interactions between two trigonal-bipyramidal $[Cu(tren)X]^+$ units. A copper(II) dimer derived from *N,N′*-bis(2-hydroxyethyl)-2,4-pentanediimine[22] is particularly interesting because of the very short O–H–O interactions (O···O = 2.31 (1), 2.33 (1) Å) and the substantial magnetic coupling transmitted through these bridges.

This azo oxime complex is the first example of formation of a hydrogen-bonded dimer in which the metal atoms have tetrahedral coordination geometries. The monomer units each have approximate twofold symmetry and are related to each other by a crystallographic twofold axis. Hence the dimer possesses approximate D_2-222 symmetry if the question of possible asymmetric placement of the bridging hydrogen atoms is ignored. The hydrogen-bonding linkage is chiral, as can be seen in Figure 2 if one traces the bonds of this linkage in the order O···O–N–Cu–N–O···O. In the dimer depicted in Figure 2, these bond sequences (two idependent sequences are present) each describe slightly more than one turn of a left-handed helix. The corresponding right-handed helices will, of course,

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be present in the centrosymmetrically related dimer.

As is evident from Tables IV and V, there is excellent agreement between corresponding structural parameters of the two azo oxime ligands. The mean C=N and N=O distances of 1.306 (6) and 1.346 (6) Å, respectively, agree well with typical values found in metal complexes of dimethylglyoxime and other *vic*-dioximes.[23] The mean N=N distance of 1.284 (6) Å is within the range of values found for metal-bonded azo groups.[24] The ligand as a whole is very nearly planar, with only a small deviation (ca. 0.06 Å) of the methyl carbon atom and small (1.4°) twisting of the phenyl ring from the plane of the chelate ring.

The coordination about the copper atoms is distorted tetrahedral, as expected for a Cu(I) complex. The Cu–N(azo) and Cu–N(oxime) distances differ only slightly. The mean Cu–N(azo) distance of 1.996 (4) Å agrees well with the value of 1.993 (16) Å found in a copper (I) chloride–azomethane complex.[25] A shorter Cu(I)–N(azo) distance of 1.90 (2) Å has been reported in a cuprous chloride complex of a bicyclic azo ligand.[26]

The observed physical properties of the title compound and its homologues[1] are consistent with their formulation as copper(I) complexes. All members of this series are diamagnetic, as determined by magnetic susceptibility measurements and NMR spectra. The dimeric nature of a representative member of this series in benzene indicates that the hydrogen bonds remain intact in this solvent. The nature of the reduction process whereby the Cu(I) complex is obtained from the starting Cu(II) complex is unclear. This point is being investigated, as are other physical and chemical properties of this complex.[27]

Registry No. ((Phenylazo)acetaldoximato-*N,N′*)((phenylazo)acetaldoxime-*N,N′*)copper(I), 74366-53-3.

Supplementary Material Available: A table of observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Characterization of the Chromium(III) Dimer *cis*-[Hydroxotetraamminechromium(III)-μ-hydroxo-pentaamminechromium(III)] Dithionate Trihydrate, $[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2\cdot 3H_2O$

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The crystal and molecular structure of the title complex *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH](S_2O_6)_2\cdot 3H_2O$ has been determined by three-dimensional, single-crystal counter X-ray diffraction methods. The complex crystallizes in the space group *Cc* of the monoclinic system with four formula units in a cell of dimensions a = 7.395 (2) Å, b = 19.417 (10) Å, c = 16.892 (5) Å, and β = 96.86 (2)°. The structure has been refined by least-squares methods to a final value of the conventional R factor (on F) of 0.044 on the basis of 1457 independent intensities. The structure consists of *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ cations which interact through extensive hydrogen-bonding networks with the dithionate anions and the solvent molecules. The geometry around each chromium(III) center in the dimeric cation is roughly octahedral, the nine Cr–N distances falling in the range 2.055 (11)–2.111 (10) Å with an average value of 2.09 (2) Å. The terminal Cr–O bond length is 1.915 (9) Å. The Cr–O bridging distances and associated Cr–O–Cr bridging angle are 1.962 (8) Å, 1.989 (8) Å, and 142.8 (5)°. The magnetic susceptibility of the complex in the range 4–290 K indicates antiferromagnetic interaction. The data were fitted to a model assuming independent triplet, quintet, and septet energies. The results were almost consistent with the Van Vleck equation with a triplet energy of 20.56 (2) cm^{-1}. No statistical evidence was found for the necessity of a biquadratic exchange term. A similar triplet energy was found in the corresponding chloride dihydrate.

Introduction

The well-known rhodo and erythro chromium(III) dimers, first reported by Jørgensen[3] in 1882, have been the subjects of intense magnetic[4–13] and spectroscopic[14–17] interest. The weakly paramagnetic basic rhodo complex has been shown by crystallographic methods to contain a linear Cr–O–Cr linkage,[10,18,19] while the acid rhodo complex contains a bent Cr–OH–Cr unit.[12,17,18]

The magnetic properties of dimeric transition-metal complexes have been shown to be dependent upon their structures. In the simplest cases of the copper(II) complexes of formulation $[Cu(L)OH]_2^{n+}$ where L is a bidentate ligand, the magnetic-exchange parameter J has been found[20] to be de-

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