of *tert*-butyl groups, whereby the lengthening of the P–C bond is about twice as large as for the P–F bond. It should be pointed out that the variation of the P–C bond length from $\mathrm{Bu^tPF_2}$ to $\mathrm{Bu^t_3P}$ is almost 0.1 Å. The bond angles at the central phosphorus atom do not show such an obvious correlation with the number of *tert*-butyl groups. The increase of the FPF angle from $\mathrm{PF_3}$ to $\mathrm{Bu^tPF_2}$ is only 1.4° and is within the error limits. The CPF and CPC angles, however, decrease by about 3 and 4°, respectively when one fluorine atom is substituted by a *tert*-butyl group. From crude steric considerations the opposite trend would be expected. The nonbonded $F\cdots C_t$ and $C_t\cdots C_t$ distances give a plausible explanation for the observed trend in the bond angles. Both distances are remarkably constant when the number of *tert*-butyl groups is increased. Thus, the large CPC angle in $\mathrm{Bu^t_2PF}$ can be understood on the basis of the P–C bond lengths and the $C_t\cdots C_t$ nonbonded distance. The $F\cdots F$ distances do not show this constant behavior.

The geometric parameters for $\mathrm{Bu^t_2PF}$ in the gas phase agree quite well with the corresponding values for the *trans*-dibromo(di-*tert*-butylfluorophosphine)nickel(II) complex in the crystal: P–C = 1.86 (1) and 1.88 (1) Å, P–F = 1.579 (7) Å, CPF = 97.3 (0.5) and 97.9 (0.5)°, and CPC = 113.8 (0.6)°. Only the P–F distances in the gas phase and in the crystal do not agree with each other.

The effect of steric strain on the geometry of a molecule can be demonstrated very clearly by comparing the structures of trimethylphosphine[21] and tri-*tert*-butylphosphine. The P–C bond lengths increase from 1.846 (3) to 1.919 (5) Å ($\Delta r_{\mathrm{P-C}}$ = 0.073 (6) Å). The same variation has been determined for the C–C bond length in isobutane[22] and tri-*tert*-butylmethane,[20] which increases from 1.535 (1) to 1.611 (5) Å ($\Delta r_{\mathrm{C-C}}$ = 0.076 (5) Å). However, the effect on the bond angles is much stronger in the phosphines, where an increase of 11.3 (0.8)° (from 98.6 (0.3) to 109.9 (0.7)°) is observed, whereas the difference is only 5.8 (0.5)°(110.9 (0.2)° for $\mathrm{Me_3CH}$ and 116.0 (0.4)° for $\mathrm{Bu^t_3CH}$) for the methane derivatives. The CPC bond angles in tri-*tert*-butylphosphine indicate that the steric interactions between two *tert*-butyl groups are very similar to the steric interactions between a *tert*-butyl group and the lone electron pair.

Registry No. $\mathrm{Bu^tPF_2}$, 29149-32-4; $\mathrm{Bu^t_2PF}$, 29146-24-5; $\mathrm{Bu^t_3P}$, 13716-12-6.

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Crystal and Molecular Structure of (Cyanato-*N*)[difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borato]copper(II), Cu(cyclops)(NCO)

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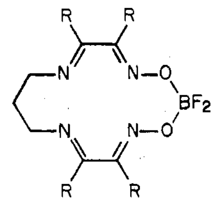
The crystal and molecular structure of Cu(cyclops)(NCO) (cyclops = difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate), $[\mathrm{Cu(C_{11}H_{18}N_4O_2BF_2)(NCO)}]$, has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The dark green crystals are monoclinic, space group $P2_1/c$ (No. 14), with four formula units in a unit cell of dimensions a = 13.552 (4) Å, b = 11.818 (4) Å, c = 11.634 (5) Å, and β = 113.69 (1)°. The structure was refined by full-matrix least-squares methods to an R value of 0.045 (R_w = 0.050) for 1528 independent reflections with $F^2 > 3\sigma(F^2)$. The coordination geometry about the copper(II) ion in the neutral monomeric complex is based on a square pyramid. While the Cu–N bonds to the macrocycle exhibit bond lengths in the normal range (1.990 (5)–2.009 (5) Å), the displacement of the copper(II) ion above the least-squares plane through these four nitrogen atoms is very large (0.58 Å). This extremely large axial displacement of the copper(II) ion is accompanied by formation of an unusually strong bond to the axial cyanato-*N* ligand, with the Cu–N1(cyanate) distance found to be 2.038 (6) Å. This very short axial bond is felt to be a consequence of the unique electronic and steric properties of this unusual uninegative macrocyclic ligand.

Introduction

Transition-metal complexes of the macrocyclic ligand difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate (**1**, R = $\mathrm{CH_3}$, hereafter referred to as cyclops) and related ligands of the general formulation **1**, together with complexes of the precursor dioxime ligands of these macrocycles, have recently been the subjects of several chemical and structural studies.[1-6] The studies of the difluoro–borate



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macrocyclic complexes, in particular, have emphasized the unusual chemical and structural properties of these species.[2,3,5]

Recently, a series of bridged dimeric complexes involving cyclops (**1**, R = CH_3) have been synthesized.[7] Members of this series of dimeric complexes $\{[Cu(cyclops)]_2L\}X$ exhibit interesting magnetic effects associated with electron spin exchange between the copper(II) ions. In addition, monomeric complexes [Cu(cyclops)L], where L = cyanate, cyanide, iodide, etc., have been synthesized.

The structures of these complexes of copper(II) are of interest for several reasons. The magnetic effects observed in the dimeric complexes make the structural properties of the bridged species of particular interest. The ready formation of complexes, both monomeric and dimeric, with "soft" ligands of high reducing power, such as the cyanide ion, puts cyclops in the relatively small class of "stabilizing ligands" which have been shown to be capable of preventing reduction of Cu(II) to Cu(I) by these "soft" ligand species.[8] In addition to these properties, there have been indications, particularly in a recent structural determination of a copper(I) carbonyl complex of cyclops by Gagné and co-workers,[5] that cyclops may be capable of imposing some very unusual structural consequences on transition-metal ions. Although one might expect such a macrocycle to allow a five-coordinate square-pyramidal geometry about copper(II), Gagné's report, together with the observation of the facile formation of unusually stable bridges involving only single-bridging species between copper(II) ions in the dimers, hints that the square-pyramidal stereochemistry of these complexes may suffer a high degree of distortion to allow the formation of unusually strong bonds to the nonmacrocyclic ligands in the axial positions. To determine whether this was indeed the case, we have determined the crystal and molecular structure of (cyanato-*N*)[difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borato]-copper(II), Cu(cyclops)(NCO). The structure of this monomeric complex will also serve as a reference structure in our planned investigation of the structures of the series of dimeric Cu(II)–cyclops complexes referred to above.

Experimental Section

Crystals of the title compound were kindly supplied by Dr. Mark Wicholas.

Crystal Data. For $[Cu(C_{11}H_{18}N_4O_2BF_2)(NCO)]$ (mol wt 392.65, monoclinic): $a = 13.552$ (4) Å, $b = 11.818$ (4) Å, $c = 11.634$ (5) Å, $\beta = 113.69$ (1)°, $V = 1706.3$ Å^3; $\rho_{obsd} = 1.55$ g cm^{-3} (by neutral buoyancy in acetone–carbon tetrachloride), $\rho_{calcd} = 1.53$ g cm^{-3}; $Z = 4$, $F(000) = 804$; space group $P2_1/c$; Mo Kα radiation, λ_1 0.709 30 Å, λ_2 0.713 59 Å, μ(Mo Kα) = 13.7 cm^{-1}.

Data Collection and Reduction. Preliminary Weissenberg and precession photographs revealed only Laue symmetry $2/m$, consistent with the monoclinic crystal system. The photographic record also exhibited the systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with the monoclinic space group $P2_1/c$ (No. 14).[9]

The small, dark green crystal chosen for data collection was mounted on the Enraf–Nonius CAD-3 diffractometer, with the *c* axis approximately coincident with the diffractometer ϕ axis. After accurate centering, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations[10] on the automatically determined 2θ, χ, and ϕ settings of 35 reflections (at ambient temperature, 20 ± 1 °C) with 2θ values in the range 20–24°.

The intensities of 2533 unique reflections with $4.50 < \theta < 24.00°$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. No reflections with lower θ values were measured, since such data could suffer cutoff of the diffracted beam at the low-θ end of the scan by the beam stop. The scan range employed was 0.5° (in θ) to either side of the K$\bar{\alpha}$ peak position, at a constant scan rate of 10° min^{-1}. The number of times a given reflection was scanned varied according to the intensity, with weak reflections being scanned a maximum of four times. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and zirconium foil attenuators were inserted automatically (to avoid coincidence losses) if the peak count rate exceeded 2500 counts s^{-1}. The intensity of one of three reference reflections (006, $\bar{6}00$, and $0\bar{6}0$) was measured every 25 reflections. None of these control reflections showed any significant or systematic changes in intensity during the course of data collection.

Lorentz and polarization corrections were applied to the observed data. The uncertainty parameter *g* in the formula used for the standard deviation in the intensity[8,12] was taken as 0.04. Reflections for which $F^2 > 3\sigma(F^2)$ were judged to be observed, and the 1528 reflections which met this criterion were employed in the solution and refinement of the structure. Due to the low absorption coefficient ($\mu = 13.7$ cm^{-1} for Mo Kα radiation) and the small size and regular shape of the data collection crystal (a parallelepiped measuring 0.25 × 0.25 × 0.25 mm), no absorption correction was applied to the data.

Solution and Refinement of the Structure. The position of the copper(II) ion was assigned from the double-intensity nonorigin peaks appearing in the Harker sections of the Patterson map. The positions of all nonhydrogen atoms were then obtained from a Fourier synthesis phased by the copper(II) ion. Scattering factors for copper(II), carbon, nitrogen, oxygen, boron, and fluorine were taken from ref 13. Scattering factors for spherically bonded hydrogen atoms[14] were also taken from ref 13, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper.

Two cycles of full-matrix least-squares refinement (on *F*) with isotropic thermal parameters for all atoms were followed by three cycles of full-matrix refinement with anisotropic thermal parameters for all nonhydrogen atoms. This refinement lowered R $(=[\sum||F_o| - |F_c||/\sum|F_o|])$ from its initial value of 0.402 to 0.053 (unobserved reflections not included) and R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2})$ from 0.476 to 0.063. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight $(=4F_o^2/\sigma^2(F_o^2))$. At this point, a difference Fourier map revealed the presence of the hydrogen atoms of the macrocyclic ligand. These hydrogen atoms were then included in fixed calculated positions 0.95 Å away from carbon, with isotropic thermal parameters 1 Å^2 larger than that of the carbon atom to which they were attached. The positions of the hydrogen atoms on the methyl groups represent the results of a least-squares fit (idealized tetrahedral geometry) to the hydrogen atom positions observed in the difference Fourier map. Two further cycles of full-matrix least-squares refinement reduced R to its final value of 0.045 and R_w to 0.050. On the final cycle of refinement, no shift in any parameter was greater than 35% of the estimated standard deviation in that parameter, with most positional shifts less than 10% of the esd for the parameter concerned. An extinction correction was not deemed necessary. The highest peak in the final difference Fourier map calculated at this point was located approximately 0.5 Å from the copper(II) ion position, and no peaks of chemical significance appeared in this map. In particular, no evidence for one-half molecule of methanol of crystallization was found in the asymmetric unit, although chemical microanalysis had suggested its presence.[7]

It was initially assumed that the cyanate ion was bonded to copper(II) through nitrogen. This assumption was checked at the termination of refinement by removing the nitrogen and oxygen atoms of the cyanate ligand from the atom list, performing a structure factor calculation on the remaining atoms, and calculating a difference Fourier map. At the position closest to the copper(II) ion, a peak corresponding to 4.1 e Å^{-3} was observed, while at the position originally assigned to oxygen, a peak corresponding to 4.2 e Å^{-3} was observed. Since the terminal atom of the cyanate ion is executing much larger thermal motion than is the atom bound to copper(II), the above observation is taken to be strongly supportive of the structural assignment of the cyanate ion as an N-bonded cyanato ligand in this complex.

Final atomic positional parameters and isotropic thermal parameters are listed in Table I. Anisotropic thermal parameters are listed in Table II.

Table I. Fractional Atomic Coordinates[a]

Atom	x	y	z
Cu(II)	0.25210 (6)	0.08660 (6)	0.02391 (8)
N1	0.1703 (5)	−0.0120 (6)	−0.1285 (6)
C1	0.1462 (6)	−0.0766 (7)	−0.2071 (7)
O1	0.1187 (6)	−0.1436 (6)	−0.2931 (6)
N2	0.2264 (4)	0.2510 (4)	−0.0225 (5)
N3	0.1412 (4)	0.1231 (5)	0.0913 (5)
N4	0.3253 (5)	−0.0260 (5)	0.1585 (5)
N5	0.4054 (4)	0.1088 (4)	0.0469 (4)
O2	0.2833 (4)	0.3168 (4)	−0.0694 (4)
O3	0.4422 (3)	0.1900 (3)	−0.0090 (4)
B1	0.3565 (6)	0.2521 (7)	−0.1116 (8)
F1	0.4114 (3)	0.3326 (4)	−0.1493 (4)
F2	0.2983 (3)	0.1791 (3)	−0.2075 (3)
C2	0.1616 (5)	0.3018 (5)	0.0180 (6)
C3	0.1442 (6)	0.4269 (6)	0.0117 (7)
C4	0.1105 (5)	0.2260 (6)	0.0794 (6)
C5	0.0319 (6)	0.2755 (6)	0.1260 (7)
C6	0.1050 (6)	0.0380 (7)	0.1586 (7)
C7	0.1479 (7)	−0.0755 (8)	0.1560 (9)
C8	0.2664 (7)	−0.0945 (7)	0.2162 (8)
C9	0.4282 (6)	−0.0261 (5)	0.2009 (6)
C10	0.5021 (6)	−0.0959 (7)	0.3093 (7)
C11	0.4765 (5)	0.0561 (5)	0.1402 (6)
C12	0.5946 (5)	0.0782 (6)	0.1901 (7)
H1C3	0.2117	0.4644	0.0383
H2C3	0.1003	0.4480	−0.0724
H3C3	0.1092	0.4475	0.0650
H1C5	0.0695	0.3025	0.2091
H2C5	−0.0054	0.3364	0.0727
H3C5	−0.0183	0.2189	0.1250
H1C6	0.1278	0.0610	0.2436
H2C6	0.0285	0.0346	0.1209
H1C7	0.1159	−0.1250	0.1957
H2C7	0.1246	−0.0964	0.0701
H1C8	0.2912	−0.0756	0.3023
H2C8	0.2802	−0.1723	0.2080
H1C10	0.4852	−0.0835	0.3801
H2C10	0.4929	−0.1737	0.2869
H3C10	0.5746	−0.0743	0.3290
H1C12	0.6295	0.0161	0.1704
H2C12	0.6072	0.1452	0.1530
H3C12	0.6218	0.0874	0.2786

[a] Estimated standard deviations are given in parentheses. If no esd is reported, the parameter was not refined during the least-squares calculations.

Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cu(II)	45 (1)	51 (1)	73 (1)	4 (1)	20 (1)	2 (1)
N1	70 (5)	84 (6)	105 (8)	−15 (5)	37 (5)	−29 (6)
C1	66 (6)	66 (6)	86 (8)	−8 (6)	36 (6)	10 (7)
O1	173 (7)	118 (7)	139 (8)	−36 (6)	66 (6)	−53 (6)
N2	56 (4)	50 (4)	58 (5)	8 (4)	18 (4)	2 (4)
N3	46 (4)	77 (6)	70 (6)	−6 (4)	20 (4)	0 (4)
N4	64 (5)	51 (5)	98 (7)	4 (4)	34 (5)	16 (5)
N5	45 (4)	45 (5)	63 (5)	2 (3)	19 (4)	−2 (4)
O2	78 (4)	47 (4)	89 (5)	7 (3)	48 (4)	10 (4)
O3	49 (3)	58 (4)	82 (5)	−4 (3)	26 (3)	8 (4)
B1	63 (6)	56 (7)	65 (8)	7 (6)	24 (6)	6 (6)
F1	93 (4)	86 (4)	147 (6)	18 (3)	71 (4)	48 (4)
F2	77 (3)	88 (4)	68 (4)	17 (3)	22 (3)	−4 (3)
C2	50 (5)	56 (6)	67 (7)	7 (4)	17 (5)	−15 (5)
C3	95 (7)	64 (6)	123 (9)	21 (6)	50 (7)	−15 (6)
C4	36 (5)	74 (7)	75 (8)	3 (5)	10 (5)	−22 (6)
C5	59 (5)	96 (8)	130 (10)	10 (5)	46 (6)	−12 (7)
C6	71 (6)	93 (7)	93 (9)	−7 (6)	32 (6)	4 (6)
C7	116 (9)	86 (8)	211 (13)	0 (7)	98 (9)	37 (9)
C8	89 (7)	97 (8)	161 (11)	0 (7)	56 (7)	72 (8)
C9	57 (6)	52 (6)	72 (7)	20 (5)	20 (5)	10 (5)
C10	88 (7)	103 (8)	101 (8)	22 (6)	30 (6)	39 (8)
C11	44 (5)	43 (5)	61 (7)	8 (4)	12 (5)	−7 (4)
C12	52 (5)	70 (6)	104 (8)	5 (5)	19 (5)	−1 (6)

[a] Estimated standard deviations are given in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

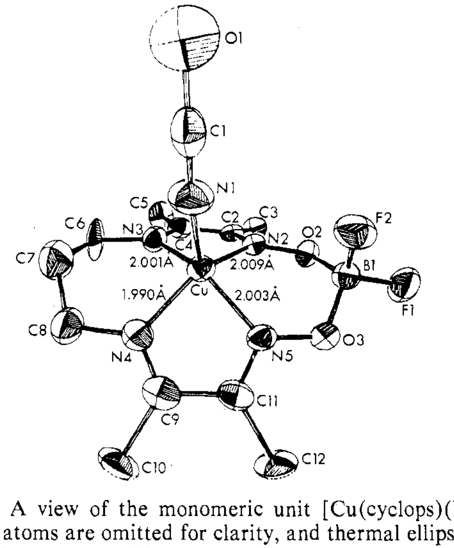

Figure 1. A view of the monomeric unit [Cu(cyclops)(NCO)]. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

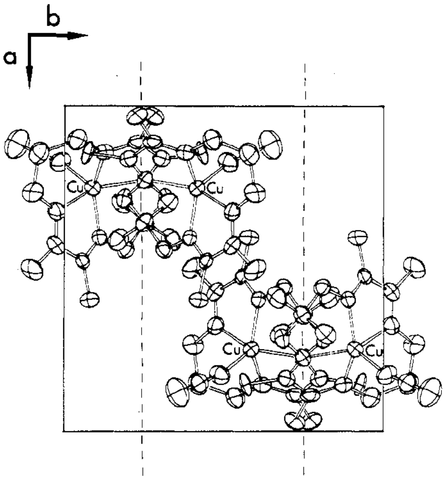

Figure 2. A view of the contents of the unit cell for [Cu(cyclops)(NCO)], looking down the c axis. Dashed lines represent the crystallographic glide planes.

Results and Discussion

The crystals consist of discrete, neutral, monomeric units of the compound Cu(cyclops)(NCO), with no significant interactions (other than van der Waals contacts) between the molecules. In particular, no chemically significant intermolecular contacts involving either Cu(II) or O1 of the cyanato-*N* group can be found within a distance of 3.5 Å from either of these atoms. The structure of one of these monomeric units is displayed in Figure 1. Figure 2, a view looking along the crystallographic glide plane, demonstrates the manner in which the molecules are arranged within the unit cell. Table III contains bond lengths and angles calculated from the atomic coordinates, while Table IV reports details of the planarity of various parts of the complex.

At first glance, the coordination geometry about the copper(II) ion seems much as expected. The nitrogen donor atoms of the macrocyclic cyclops ligand occupy the four basal sites of a square-pyramidal ligand array about copper, while the N-bonded cyanate ion occupies the apical position. The bond lengths from copper(II) to the nitrogen atoms of the cyclops ligand are normal in length,[8,15] with a mean value of 2.001 (3) Å. The four individual values (2.009 (5), 2.001 (7), 1.990 (5), 2.003 (6) Å from Cu(II) to N2–N5, respectively) are best considered equal within experimental error. Unlike the present

Table III. Bond Lengths (Å) and Angles (deg)[a]

(a) Bond Lengths Involving Cu(II)

Cu-N1	2.038 (6)	Cu-N4	1.990 (5)
Cu-N2	2.009 (5)	Cu-N5	2.003 (6)
Cu-N3	2.001 (7)		

(b) Bond Angles Involving Cu(II)

N1-Cu-N2	110.1 (2)	Cu-N1-C1	165.1 (6)
N1-Cu-N3	103.4 (3)	Cu-N2-O2	126.8 (4)
N1-Cu-N4	103.2 (2)	Cu-N2-C2	114.8 (5)
N1-Cu-N5	111.3 (3)	Cu-N3-C4	115.3 (5)
N2-Cu-N3	79.7 (2)	Cu-N3-C6	121.6 (5)
N2-Cu-N4	146.7 (2)	Cu-N4-C8	122.3 (4)
N2-Cu-N5	88.1 (2)	Cu-N4-C9	115.2 (5)
N3-Cu-N4	93.0 (3)	Cu-N5-C11	115.8 (5)
N3-Cu-N5	145.2 (2)	Cu-N5-O3	126.0 (3)
N4-Cu-N5	79.6 (2)		

(c) Bond Lengths Involving Ligand Atoms

N1-C1	1.133 (10)	N4-C9	1.278 (9)
C1-O1	1.212 (10)	C9-C10	1.503 (9)
N2-O2	1.353 (8)	C9-C11	1.498 (10)
N2-C2	1.299 (10)	C11-C12	1.490 (9)
C2-C3	1.494 (10)	C11-N5	1.286 (7)
C2-C4	1.481 (11)	N5-O3	1.361 (7)
C4-C5	1.494 (12)	O3-B1	1.483 (8)
C4-N3	1.275 (9)	O2-B1	1.485 (11)
N3-C6	1.475 (11)	B1-F1	1.384 (10)
C6-C7	1.467 (12)	B1-F2	1.379 (8)
C7-C8	1.488 (12)		
C8-N4	1.475 (12)		

(d) Bond Angles Involving Ligand Atoms

N1-C1-O1	178.4 (8)	N4-C9-C10	125.4 (7)
O2-N2-C2	117.2 (5)	N4-C9-C11	115.6 (5)
N2-C2-C3	123.8 (7)	C10-C9-C11	118.8 (6)
N2-C2-C4	114.3 (6)	C9-C11-N5	113.0 (6)
C3-C2-C4	121.8 (7)	C9-C11-C12	122.3 (5)
C2-C4-C5	118.5 (6)	C12-C11-N5	124.5 (6)
C2-C4-N3	115.7 (7)	C11-N5-O3	116.8 (5)
C5-C4-N3	125.7 (7)	N5-O3-B1	114.5 (5)
C4-N3-C6	122.9 (7)	O3-B1-O2	113.6 (6)
N3-C6-C7	113.2 (8)	O3-B1-F1	104.4 (6)
C6-C7-C8	119.3 (7)	O3-B1-F2	110.5 (6)
C7-C8-N4	112.5 (7)	O2-B1-F1	105.5 (6)
C8-N4-C9	122.0 (6)	O2-B1-F2	110.4 (6)
		B1-O2-N2	113.7 (5)

[a] Estimated standard deviations are given in parentheses.

Table IV. Least-Squares Planes

(a) Deviations from Least-Squares Planes[a]

Plane 1

Atoms determining plane: N2 (−0.013), N3 (0.020), N4 (−0.012), N5 (0.006)

Other atoms: Cu^{2+} (−0.584), O2 (0.098), O3 (0.114), B1 (−0.520), C2 (0.522), C4 (0.481), C6 (−0.016), C8 (−0.054), C7 (−0.655), C9 (0.527), C11 (0.607)

Plane 2

Atoms determining plane: N5 (−0.018), N4 (0.012), C9 (−0.008), C11 (0.034)

Other atoms: Cu^{2+} (0.143), C10 (0.013), C12 (0.212), C8 (0.099), O3 (0.094)

Plane 3

Atoms determining plane: N4 (0.005), N3 (−0.002), C8 (−0.011), C6 (0.005)

Other atoms: Cu^{2+} (−0.602), C7 (−0.616), C4 (0.453), C9 (0.543)

Plane 4

Atoms determining plane: N2 (−0.016), N3 (0.008), C4 (−0.021), C2 (0.013)

Other atoms: Cu^{2+} (0.091), C5 (−0.033), C3 (0.156), C6 (0.084), O2 (0.134)

Plane 5

Atoms determining plane: N2 (−0.002), N5 (0.004), O2 (0.005), O3 (−0.004)

Other atoms: Cu^{2+} (−0.485), B1 (−0.663), C2 (0.581), C11 (0.617)

(b) Equations of the Planes[b]

Plane no.	*A*	*B*	*C*	*D*
1	1.794	6.119	8.386	1.766
2	−3.496	8.522	8.057	−0.094
3	1.724	5.924	8.524	1.753
4	5.946	2.336	7.288	1.784
5	1.023	5.629	8.980	1.445

(c) Dihedral Angles between Planes

1-2, 28.0°; 1-3, 1.2°; 1-4, 25.7°; 1-5, 4.4°; 2-3, 28.5°; 2-4, 53.6°; 2-5, 27.5°; 3-4, 25.2°; 3-5, 3.5°; 4-5, 26.5°

[a] The number given for each atom represents the distance, in Å, of that atom from the calculated plane. [b] In the form $Ax + By + Cz = D$.

case, other studies have shown distinctly unequal pairs of Cu–N bond lengths in similar systems. In a study of the copper(I) complex Cu(cyclops)(CO),[5] the Cu–N bond lengths were found to be divided into two distinct pairs (2.164, 2.104 Å). A structural study[4] of a closely related copper(II) complex, perrhenato-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II), in which the macrocycle is only partly unsaturated (compared with cyclops) and is not closed by the BF_2 moiety, also showed two distinctly different pairs of copper–nitrogen bond lengths, with Cu–N(amine) found to be 1.99 (1) Å and Cu–N(oxime) 1.96 (1) Å. Other complexes involving closely related ligand systems bound to different metal ions also show this dichotomy of metal–nitrogen bond lengths. The structures of the rhodium(III) complexes *trans*-methyliodo[difluoro[3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)]borate]rhodium(III)[16] and *trans*-bis(phenyl selenido)[difluoro-3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(III)[3] exhibited Rh–N(oxime) distances ~0.03 Å shorter than the other pair of Rh–N distances. The structure of the cobalt(III) complex of the noncyclized dioxime precursor of cyclops, *trans*-dimethyl[3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)]cobalt(III),[1] also showed this same trend. The same dichotomy may also be observed, although perhaps not as distinctly, in the Cu–N(imine) and Cu–N(oxime) bond lengths of a copper(II) complex of the noncyclized dioximate precursor of cyclops itself.[6] These observed systematic inequalities in metal–nitrogen bond lengths thus seem to be a function of the relative donor abilities of the two types of nitrogen atom within the macrocycle, and the reason that such a distinct dichotomy is not observed in the Cu(II)–N bond lengths of the present structure is not clear. It may be noted that the Cu(II)–N bond lengths in the complex formed from the noncyclized cyclops precursor[6] are distinctly shorter than those observed here for Cu(cyclops)(NCO). Apparently the final cyclization to yield the macrocyclic ligand constrains the system so as to produce slightly less favorable bonding to copper(II) than is possible with the uncyclized dioxime ligand.

More detailed examination of the square-pyramidal copper(II) coordination geometry in the present structure does reveal some surprising features. In such a coordination environment, the copper(II) ion is typically displaced 0.2–0.3 Å out of the mean plane of the basal coordinating atoms toward the apical position.[15] In Cu(cyclops)(NCO), the corresponding displacement amounts to 0.58 Å! This very large displacement could not have been predicted from the earlier structural work, as in the six-coordinate cobalt(III) and rhodium(III) complexes[1,3,16] the metal ions were found to lie in the plane of the macrocyclic nitrogen atoms. Since the ionic radii of Cu(II) and Rh(III) are very similar,[17] the size of the metal ion cannot be the controlling factor in this severe distortion. While the population of the $d_{x^2-y^2}$ orbital in the d^9 copper(II) case undoubtedly plays a role in making the out-of-plane position more favorable, the copper(II) ion in the closely related perrhenato complex of the uncyclized (and partially saturated) dioximato ligand[4] was found to be only 0.24 Å out of the basal plane of nitrogen atoms, and in the copper(II) complex of the noncyclized dioximate precursor of cyclops, the out-of-plane displacement is only 0.13 Å.[6] Rather large conformational changes of the macrocyclic ligand also accompany this severe out-of-plane distortion (see below). An even more dramatic distortion of this type was seen in the structure of the d^{10} copper(I) species Cu(cyclops)(CO),[5] where the cuprous ion was observed to lie 0.96 Å above the basal plane of nitrogen atoms.

The extremely large out-of-plane displacement of the copper(II) ion in the Cu(cyclops)(NCO) complex apparently allows the formation of an unusually strong bond to the cyanato-*N* ligand in the apical position, despite the fact that the Cu–N(macrocycle) bonds are still of normal strength (as reflected in the bond lengths, vide supra). The normal square-pyramidal coordination environment about copper(II) involves a bond to the apical ligand which is typically 0.2–0.6 Å longer than the bonds to the basal atoms.[15] In the present case, however, the Cu–N(cyanate) bond length is observed to be only 2.038 (6) Å, which is less than 0.04 Å longer than the mean Cu–N(macrocycle) bond length!

The chemical literature contains a surprising lack of true structural information on isocyanate groups bound in a terminal fashion to copper(II). The only viable comparisons of the above bond length would seem to be to the Cu–N(isocyanato) bond lengths in the polymeric complex Cu$(NCO)_2$(2,4-lutidine)[18] (where Cu–N(cyanato) bond lengths from 1.98 to 2.46 Å were seen for the bridging cyanate groups) and to Cu(II)–N(isothiocyanato) bond lengths. In the latter category, perhaps the most relevant structure is that of the complex ion [Cu(*N*-methylethylenediamine)$_2$(NCS)], where the apical Cu–N(isothiocyanato) bond length was observed to be 2.24 (1) Å.[19] Only in cases where the isothiocyanato ligand was found bonded in the basal plane of a square pyramid about Cu(II) are observed Cu–N bond lengths as low as 2.0 Å.[20] The extremely short Cu–N(cyanato) bond length observed in the present structure seems to present a unique situation for apically bonded ligands in this coordination environment.

The cyanato-*N* ligand itself exhibits a normal atomic configuration for terminal transition-metal N-bonded cyanate complexes. Hendrickson[21] has reviewed the pertinent literature, which shows terminally bound, nonbridging cyanato-*N* groups to exhibit M–N–C angles of 172–180° (linear), N–C bond lengths of 1.12–1.15 Å (triple bonds), and C–O distances of 1.18–1.24 Å. The N–C (1.13 (1) Å) and C–O (1.21 (1) Å) distances observed here in Cu(cyclops)(NCO) fit nicely into this pattern, despite the apparent lack of linearity in the copper–cyanato-*N* system (Cu–N–C 165.1 (6)°). This lack of linearity may be due to the influence of the BF_2 moiety, since F2 approaches both copper(II) and N1 of the cyanate group rather closely (Cu–F2 3.192 (5) Å, N1–F2 3.200 (8) Å). The importance of this interaction can also be seen in the fact that the cyanato-*N* ligand is not directly over the copper(II) ion but is displaced slightly in the direction of the propylene linkage of the macrocycle. This is clearly evident from the two distinct sets of N1–Cu–N(macrocycle) angles observed in this complex (average N1–Cu–N(oxime) angle of 110.7° vs. an average value of 103.3° for the two N1–Cu–N(imine) angles).

Bond lengths observed for the cyclops ligand itself have essentially the same values as the corresponding bond lengths of the very similar ligand in the previously discussed rhodium(III) complexes.[3,16] There are, however, major differences in the conformations of the macrocycles between the Cu(cyclops)(NCO) case and these earlier complexes. In the six-coordinate Rh(III) structures, the macrocycle was largely planar, with the exception of the central atom of the propylene bridge and the boron atom closing the macrocycle, which deviated from the macrocyclic plane strongly (~0.5 Å out of plane) in *opposite* directions. In the five-coordinate Cu(cyclops)(NCO), however, the macrocycle is distinctly nonplanar. If the plane of the coordinating atoms N2–N5 is adopted as a reference plane (plane 1 in Table IV), the unsaturated portions of the macrocycle (planes 2 and 4, Table IV) make dihedral angles of 28 and 26° with the reference plane, thus presumably allowing the lone pairs of the nitrogen atoms to be directed more effectively toward the copper(II) ion (note that Cu(II) is only ~0.1 Å out of planes 2 and 4). In strong contrast to the structures of the Rh(III) complexes referred to above, the central atom of the propylene bridge and the boron atom in Cu(cyclops)(NCO) are found *on the same side* of the reference plane. Both of these atoms are displaced in the direction of N1 of the isocyanate group. This rather surprising result is presumably a consequence of the combined effects of the distorted five-coordinate geometry and the changes in the macrocycle geometry necessary to maintain effective bonding to the copper(II) ion. Thus, the atoms B1, N2–N5, and C7 exhibit a "boat" configuration in the Cu(cyclops)(NCO) complex, in contrast to the "chair" conformation of the corresponding atoms in the six-coordinate metal complexes.

The present study has thus shown cyclops to be a rather flexible macrocycle, rather than the rigid system suggested by earlier studies.[16] Cyclops has also been shown to be a ligand capable of allowing rather unique bonding parameters to be seen about the copper(II) ion. These unique bonding parameters will presumably also be made manifest in the structural properties of the bridged copper(II)–cyclops complexes which will be determined in the near future.

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Supplementary Material Available: Table V listing structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of New Metal–Metal Bonded Species. 2. Crystal and Molecular Structure of Dimeric Niobium(III) and Tantalum(III) Bromide Adducts with Tetrahydrothiophene. Direct Stereochemical Evidence of Bonding Electron Density in Confacial Bioctahedra with Metal–Metal Double Bonds

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The previously reported niobium dimer $Nb_2Br_6(SC_4H_8)_3$ and the recently prepared tantalum analogue $Ta_2Br_6(SC_4H_8)_3$ have been characterized by complete structure determinations. Both compounds exist in the solid state as molecular confacial bioctahedrons with the two metal atoms of each dimer displaced from the center of their idealized octahedra toward one another. The Nb–Nb distance of 2.728 (5) Å and the Ta–Ta distance of 2.710 (2) Å are in accord with a formal metal–metal double bond. A distinctive feature of the structures is the unusually close approach of the two bromines in bridging positions of the confacial bioctahedra; this separation of only 3.30 Å is attributed to stereochemical activity of the two metal–metal π-bonding electrons. $Nb_2Br_6(SC_4H_8)_3$ crystallized in $P\bar{1}$ space group with $Z = 2$ and $\rho(\text{calcd}) = 2.49$ g cm^{-3} for a unit cell of dimensions $a = 15.088$ (8) Å, $b = 12.121$ (6) Å, $c = 8.981$ (2) Å, $\alpha = 112.93$ (3)°, $\beta = 77.32$ (2)°, and $\gamma = 125.23$ (2)°. Least-squares refinement of the structure resulted in a conventional agreement factor R_1 of 0.109 for 1870 reflections having $F^2 > 3\sigma(F^2)$. Crystals of $Ta_2Br_6(SC_4H_8)_3$ belonged to the $P\bar{1}$ space group with $Z = 2$ and $\rho(\text{calcd}) = 2.98$ g cm^{-3}. The cell dimensions were $a = 12.08$ (1) Å, $b = 12.74$ (1) Å, $c = 8.98$ (1) Å, $\alpha = 83.98$ (5)°, $\beta = 112.45$ (5)°, and $\gamma = 105.40$ (5)°. An R factor of 0.069 resulted from least-squares refinement of 1930 data points with $F > 3\sigma(F)$.

Introduction

The chemistry of the lower oxidation states of niobium and tantalum in discrete complexes remains relatively unexplored. The first structurally characterized halide complexes of niobium(III) were reported in 1970 as the metal–metal bonded binuclear salts $M_3Nb_2X_9$[2] (M = Rb, Cs; X = Cl, Br, I). Subsequently the molecular complexes $Nb_2X_6(SC_4H_8)_3$ (X = Cl, Br, I) were prepared and characterized by spectroscopic methods.[3] It was concluded that the molecules possessed the confacial bioctahedral structure with the S atom of one unique tetrahydrothiophene ligand occupying one of the three bridging positions. Magnetic data showed the compounds to be diamagnetic and a strong Nb–Nb interaction was inferred. In contrast, well-characterized tantalum(III) halide compounds are virtually unknown and therefore of considerable interest. A successful synthetic route to the tantalum dimers $Ta_2X_6(SC_4H_8)_3$ (X = Cl, Br) has been developed.[4] Physical methods of characterization showed that the tantalum compounds were entirely analogous to those of niobium. X-ray structural determinations of both $Nb_2Br_6(SC_4H_8)_3$ and $Ta_2Br_6(SC_4H_8)_3$ were undertaken in order to clearly delineate any differences between them. In related complexes of molybdenum(III) and tungsten(III) containing the anions $M_2X_9^{3-}$ the W–W distance is much shorter, 2.41 Å in $K_3W_2Cl_9$,[5] than the Mo–Mo distance in $Cs_3Mo_2Cl_9$,[6] 2.66 Å. Therefore it was of great interest to see if the Ta–Ta and Nb–Nb bond lengths would differ so markedly.

Experimental Section

The two compounds were prepared according to methods described elsewhere.[3,4] Crystals suitable for x-ray data collection were obtained by recrystallization of the materials from toluene solutions which had been saturated at room temperature, filtered, and cooled slowly to ca. −15 °C to induce crystal growth. The very air-sensitive crystals were then sealed in Lindemann glass capillaries under nitrogen.

Data Collection and Reduction. Crystals of both $Nb_2Br_6(SC_4H_8)_3$ and $Ta_2Br_6(SC_4H_8)_3$ were examined by precession and Weissenberg film techniques and both exhibited $\bar{1}$ Laue symmetry indicating a triclinic space group. No systematic absences were observed. Lattice parameters were determined for the niobium compound by least-squares fit to 12 independent reflection angles whose centers were determined by left–right, top–bottom beam splitting on a previously aligned Hilger-Watts four-circle diffractometer (Cu Kα radiation, λ 1.5418 Å). Any error in the instrumental zero was eliminated by centering the reflection at both $+2\theta$ and -2θ. For the tantalum compound a similar procedure was used, but only three independent reflection angles and Mo Kα radiation (λ 0.71069 Å) were employed. The following lattice parameters were found: for $Nb_2Br_6(SC_4H_8)_3$ $a = 15.088$ (8) Å, $b = 12.121$ (6) Å, $c = 8.981$ (2) Å, $\alpha = 112.93$ (3)°, $\beta = 77.32$ (2)°, and $\gamma = 125.23$ (2)° with $Z = 2$ and $\rho(\text{calcd}) = 2.49$ g cm^{-3}; for $Ta_2Br_6(SC_4H_8)_3$ $a = 12.08$ (1) Å, $b = 12.74$ (1) Å, $c = 8.98$ (1) Å, $\alpha = 83.98$ (5)°, $\beta = 112.45$ (5)°, and $\gamma = 105.40$ (5)° with $Z = 2$ and $\rho(\text{calcd}) = 2.98$ g cm^{-3}.

The crystals chosen for data collection had approximate dimensions as follows along the a, b, and c axes, respectively: for $Nb_2Br_6(SC_4H_8)_3$ 0.270, 0.050, and 0.045 mm and for $Ta_2Br_6(SC_4H_8)_3$ 0.06, 0.08, and 0.40 mm. Integrated intensities were measured using Ni-filtered Cu Kα and Zr-filtered Mo Kα radiation, respectively, for the niobium and tantalum compounds, using the θ–2θ scanning technique on the automated diffractomer cited earlier. A counting rate of 0.2048 s per step of 0.01° in θ was employed with a variable scan range of 50 steps plus two steps per degree θ. Stationary crystal, stationary counter background measurements were made at the beginning and end of each scan for half the total scan time. All data were collected within a 2θ sphere of 55° for the niobium and 45° for the tantalum compounds, respectively, in each of four octants; a total of 3500 and 3216 reflections were monitored in the respective cases.

As a general check on electronic and crystal stability the intensities of three standard reflections were measured every 50 reflections during the data collection period. For the niobium compound the total decrease in intensity of these reflections was only 15% and the data were appropriately corrected. However, for the tantalum compound the intensities of the standard reflections decreased to only 20% of the original intensities by termination of data collection. A linear least-squares fit of standard intensities vs. the number of data points monitored (n) was made using a weighting factor of $1/C_t$ for the intensities (C_t = total counts). The correlation coefficient was >0.99

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