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Stabilization of High Oxidation States by Strong Electron-Donating Ligands. Crystal Structure and Properties of Tetra-*n*-butylammonium *o*-Phenylenebis(biuretato)cuprate(III)–Chloroform, $(n\text{-}C_4H_9)_4NCu[o\text{-}C_6H_4(NCONHCONH)_2]\cdot CHCl_3$

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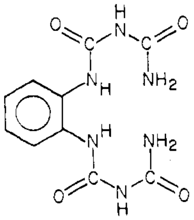
The Cu^{III} complex of *o*-phenylenebis(biuret) can be obtained by oxidation of the parent Cu^{II} complex with iodine. Tetra-*n*-butylammonium *o*-phenylenebis(biuretato)cuprate(III)–chloroform, $(n\text{-}C_4H_9)_4NCu[o\text{-}C_6H_4(NCONHCONH)_2]\cdot CHCl_3$, crystallizes with a triclinic unit cell, $a = 9.68$ (1) Å, $b = 10.75$ (1) Å, $c = 16.64$ (4) Å, $\alpha = 93.4$ (1)°, $\beta = 105.2$ (1)°, $\gamma = 94.32$ (5)°, and $V = 1660$ (8) Å^3; $d_{\text{measd}} = 1.44$ g cm^{-3} and $d_{\text{calcd}} = 1.403$ g cm^{-3} for $Z = 2$. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares to a residual of 0.079 for 3075 independent reflections whose intensities were measured on an automatic diffractometer. The Cu atom is planar coordinated by four deprotonated amide nitrogen atoms. The Cu^{III}–N bond lengths (1.82–1.89 Å) are shorter than the Cu^{II}–N distances in related Cu^{II} complexes and comparable with Ni^{II}–N(peptide) bond lengths. This is an indication that Cu^{III} (d^8) is the correct description for the oxidation state of the metal. The unusual redox behavior, coordination geometry, magnetic properties, and reactivity of Co, Ni, or Cu complexes with biuret or peptides can be understood on the basis of strong electron donation by the deprotonated amide groups and redox processes at the metal center. Electrochemical and NMR data for the complex are reported.

Introduction

In previous publications[1-3] the synthesis and physical properties of complexes of tervalent Cu, Ni, or Co with ligands coordinating via deprotonated amide groups were reported. Stable bis(bidentate)-chelated Cu^{III} complexes were prepared with biuret (H_2N–CO–NH–CO–NH_2, biH_2)[4], 3-propylbiuret (H_2N–CO–N(C_3H_7)–CO–NH_2), and oxamide (H_2N–CO–CO–NH_2). Only the complexes with alkyl-substituted biuret are soluble (e.g., in dimethyl sulfoxide, acetone, and ethanol). Spectroscopic, magnetic, and polarographic data were shown to be consistent with planar bis(bidentate) chelation of the Cu atom by two $(HN\text{–}CO\text{–}NR\text{–}CO\text{–}NH)^{2-}$ ligands (R = H or –C_3H_7).[2] The crystal structure analysis of the parent Cu^{II} complex $K_2Cu(bi)_2\cdot 4H_2O$ had previously revealed this type of metal coordination.[5] It has also been found in paramagnetic Co^{III} complexes with 3-phenylbiuret[6] and 3-*n*-propylbiuret[7] [$(HN\text{–}CO\text{–}NR\text{–}CO\text{–}NH)^{2-}$ with R = C_6H_5 and *n*-C_3H_7, respectively]. Crystals of a Cu^{III}–biuret complex suitable for x-ray diffraction could previously not be obtained.

Metal binding via deprotonated amide groups also occurs in complexes with amino acid amide and peptide ligands, and these species may be oxidized to the corresponding Cu^{III} complexes.[8-11] However, no crystalline derivatives of copper(III) peptide complexes have so far been prepared, probably because these compounds are relatively unstable. A half-life of only 2 h has been reported for a solution of a copper(III) triglycylglycinato complex at 25 °C and optimum pH conditions.[11] Intramolecular ligand oxidation is followed by fragmentation of the peptide.[8,9] Recently crystals were obtained of a new Cu^{III} complex with *o*-phenylenebis(biuret) [o-C_6H_4(NH–CO–NH–CO–NH_2)$_2$, *o*-phen(bi)$_2H_4$]. We now report its x-ray crystal structure and discuss some of the properties of Co, Ni, and Cu complexes with this type of ligand.



Experimental Section

***o*-Phenylenebis(biuret)** was prepared according to the previously published method[3] with slight modifications which were found to improve the yield. *o*-Phenylenediamine (BDH, reagent grade) was recrystallized from toluene. Nitrobiuret (H_2N–CO–NH–CO–N-H–NO_2) was freshly prepared.[12] Nitrobiuret (3 g, 0.02 mol) and *o*-phenylenediamine (1.1 g, 0.01 mol) were suspended in water (35 mL). The mixture was flushed with nitrogen and stirred under nitrogen on a water bath at 70 °C for 2 h. The reagents slowly dissolved and from the clear solution *o*-phenylenebis(biuret) precipitated spontaneously or precipitated on heating the solution to 100 °C. Finally the mixture was kept at 100 °C for 15 min and the product was obtained from the hot solution by filtration and washed with cold water.

$(n\text{-}C_4H_9)_4NCu^{III}[o\text{-phen(bi)}_2]\cdot CHCl_3$. $CuCl_2\cdot 2H_2O$ (0.34 g, 2 mmol), *o*-phenylenebis(biuret) (0.56 g, 2 mmol) and I_2 (0.35 g, 0.7 mmol) were dissolved in a mixture of Me_2SO (20 mL) and water (5 mL). To this solution 5 mL of a $(n\text{-}C_4H_9)_4NOH$ solution (BDH reagent grade, 40% aqueous solution) and 5 mL of water were added. The greenish precipitate was collected by filtration on a sintered-glass filter covered with filter aid. The precipitate was dissolved in Me_2SO, the green solution was filtered, and small dark green needles of the pure

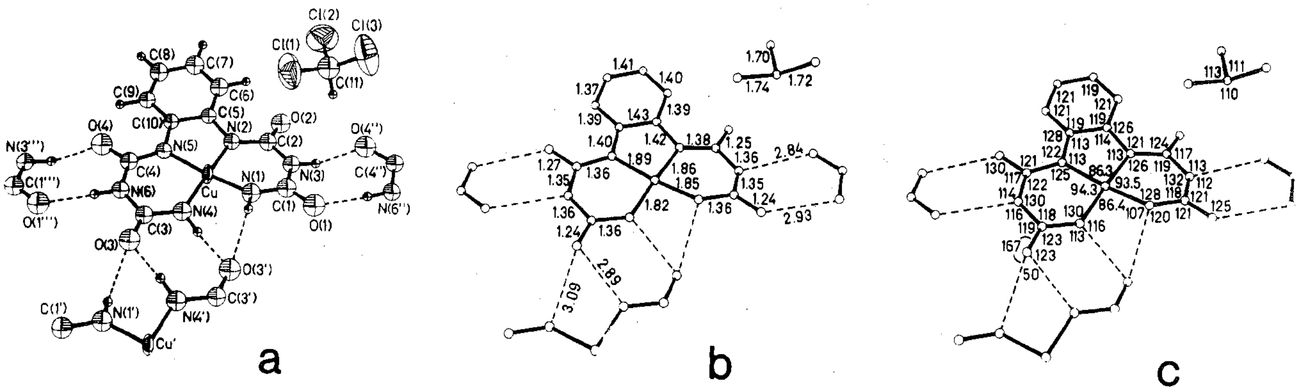


Figure 1. Labeling and dimensions of the Cu[*o*-phen(bi)$_2$]$^-$ ion and the chloroform molecule. The orientation is the same as in the right eye view of the stereodrawing (Figure 3). Hydrogen bonds are indicated with dashed lines. Part a shows the atomic labeling, anisotropic vibration ellipsoids of Cu and Cl, and isotropic vibration of the other atoms (50% probability). H atoms are not labeled and are represented as spheres with 0.1-Å radii. Superscripts refer to the following symmetry operations: none = x, y, z; $'$ = $1 - x, 1 - y, -z$; $''$ = $-1 + x, y, z$; $'''$ = $1 + x, y, z$. Part b shows the interatomic distances in Å. Estimated standard deviations are 0.01 Å for Cu–N distances and 0.02 Å for all other bond lengths. Part c shows the bond angles in degrees. Estimated standard deviations are 0.5° for angles around Cu and 1° for all other angles.

complex were obtained after addition of chloroform. The product was filtered off and washed with chloroform.

Anal. Calcd for $CuC_{27}H_{45}N_7O_4Cl_3$: C, 46.36; H, 6.20; N, 14.02. Found: C, 45.6; H, 6.5; N, 13.7. The presence of chloroform was confirmed by the mass spectrum of the compound at 120 °C.

Physical Measurements. Polarographic measurements were carried out with a Metrohm Polarecord E261 and a Metrohm *iR* Kompensator E466 using three-electrode geometry. The measurements were made in Me_2SO with 0.1 N $(n\text{-}C_4H_9)_4NClO_4$ as supporting electrolyte at 25 °C. The potentials were measured with a rotating platinum electrode vs. a saturated calomel electrode. The half-wave potential $(E_{1/2})$ of the title compound is 0.04 V ($|E_{3/4} - E_{1/4}| = 75$ mV).

The NMR spectrum at 25 °C in $Me_2SO\text{-}d_6$ with internal reference Me_4Si was measured on a Varian XL100 spectrometer. It is indicative for a diamagnetic compound; shifts in τ values, $10 + [(H - H_{ref})/H_{ref}] \times 10^6$, (intensities in parentheses): CH + NH, 1.78 (4); CH, 3.30 (2); NH, 4.40 (2). After addition of D_2O: CH, 1.80 (2); CH, 3.23 (2).

Diffraction Measurements and Data Reduction. Preliminary photographic data obtained using a Supper precession camera using Zr-filtered Mo Kα radiation indicated that the Laue symmetry was $\bar{1}$ so that the space group was $P1$ or $P\bar{1}$. The space group $P\bar{1}$ was confirmed by the solution of the structure. Photographs made with a number of crystals showed that the resolution of the diffraction data was poor ($\theta_{max} < 20°$). A needle-shaped crystal of dimensions 0.56 × 0.08 × 0.04 mm in the [1,0,0], [0,–1,1], and [0,1,1] directions, respectively, was used for data collection on a Nonius CAD-4/F automatic diffractometer. All measurements were made using graphite-monochromated (monochromator $d_{002} = 3.354$ Å) Mo Kα radiation (λ(Mo Kα_1) 0.709 30 Å, λ(Mo Kα_2) 0.713 59 Å). The takeoff angle at the tube was 2.8°. The crystal-to-counter distance was 173 mm. The vertical detector aperture was 4 mm.

Cell dimensions were obtained by least-squares refinement of the θ values of 16 automatically centered reflections ($\theta > 10°$). The lattice constants are $a = 9.68$ (1) Å, $b = 10.75$ (1) Å, $c = 16.64$ (4) Å, $\alpha = 93.4$ (1)°, $\beta = 105.2$ (1)°, $\gamma = 94.32$ (5)° and $V = 1660$ (8) Å^3. The experimental density of 1.44 (2) g cm^{-3} (determined by flotation in a $CHCl_3$–$CHBr_3$–cyclohexane mixture) agrees well with the value of 1.403 g cm^{-3} calculated for $Z = 2$. Profile analysis of representative reflections showed that the reflections were rather broad and asymmetric. This led to the selection of the ω-scan mode for the measurement of intensity data, a horizontal aperture of (1.3 + 0.35 tan θ) mm, and an ω-scan angle of (0.7 + 0.35 tan θ)°. The scan speeds were determined by a required precision of $\sigma(I) < 0.01\ I$ with a maximum scan time of 100 s/reflection. Each reflection was scanned in 96 steps. The peak (P) was taken to consist of the 64 central steps leaving 16 steps at each end of the scan to measure the backgrounds (B_1 and B_2). The intensity (I) was calculated as $I = v[P - 2(B_1 + B_2)]$, where v is a factor to account for differences in scan speed. The standard deviation of I is defined by the equation $\sigma(I) = [v(P + 4(B_1 + B_2))]^{1/2}$. The orientation of the crystal was checked after every 100 reflections and if necessary a new orientation matrix was determined. Decomposition as determined by the drop in intensity of four standard reflections measured every 10 000 s of exposure time was 7% during the period of the measurements. The decomposition was isotropic.

Lorentz and polarization corrections were applied in the usual way. The data were corrected for the observed decomposition and for absorption ($\mu = 9.43$ cm^{-1}, based on standard values taken from ref 13a). The intensities of 3075 independent reflections ($\theta < 20°$) were recorded. A complete set of equivalent data ($\bar{h},\bar{k},\bar{l}$) was measured. There were 1423 pairs of equivalent reflections with $I > 3\sigma(I)$. The unweighted discrepancy factor for these reflections, defined as $(\sum||F_h| - |F_{\bar{h}}||^2/\sum|F_{av}|^2)^{1/2}$, where $F_{av} = (|F_h| + |F_{\bar{h}}|)/2$, was 0.046. The two sets of data were averaged to give 3075 unique reflections, including 1919 with $I > 3\sigma(I)$.

Structure Determination and Refinement. The structure was solved by standard Patterson and Fourier methods.[14] Scattering factors for neutral Cu, Cl, O, N, C, and H together with anomalous dispersion terms for Cu and Cl were taken from ref 13b. An analysis of the errors in the data was made before averaging the two equivalent sets of data.[15] A third-degree polynomial was fitted to a plot of average values of $[(\Delta F)^2 - \sigma^2(F)]$ vs. F for the 1423 common observed reflections in 18 intervals of F. The polynomial coefficients were –0.463 78, 0.113 75, –0.004 55, and 0.000 63. After averaging of the two sets of data $\sigma^2(F)$ was recalculated for each reflection as the sum of the value derived from this polynomial and $\sigma^2(F)_{stat}$. The positional parameters and temperature factors of the nonhydrogen atoms were refined by full-matrix least-squares methods using the 1919 reflections with $I > 3\sigma(I)$. The function minimized was $\sum\sigma^{-2}(F)\{|F_o| - s|F_c|\}^2$. Only the temperature factors of the Cu and Cl atoms were refined anisotropically. Anisotropic refinement of other atoms was not meaningful due to the quality of the data. Hydrogen atoms were placed on their calculated positions, which were recalculated after each refinement cycle (C–H = 1.05 Å, N–H = 0.95 Å).[16] All hydrogen atoms were given a fixed isotropic temperature factor ($U_{iso} = 0.0633$ Å^{-2}). The terminal $-CH_3$ groups of the $(n\text{-}C_4H_9)_4N^+$ ion were oriented in such a way as seemed most likely from a difference Fourier map, but not all hydrogen atoms could be located. A final ΔF synthesis showed no excursions above background. The values of the residuals[17] are $R = 0.079$ and $R_w = 0.095$ for the 1919 reflections used in the refinement and $R = 0.174$ and $R_w = 0.0968$ for all 3075 reflections.

Atomic positional and thermal parameters are given in Table I. A table of calculated positions of hydrogen atoms and a list of observed and calculated structure factors are available.[18]

Description of the Structure

The structure consists of discrete $(n\text{-}C_4H_9)_4N^+$ and Cu[*o*-phen(bi)$_2$]$^-$ ions and chloroform molecules. Bond lengths and angles are given in Figures 1 and 2. The dimensions of the biuret moieties are equal (within experimental error) to those found previously in complexes of Cu(II)[19] and Co(III)[6,7]

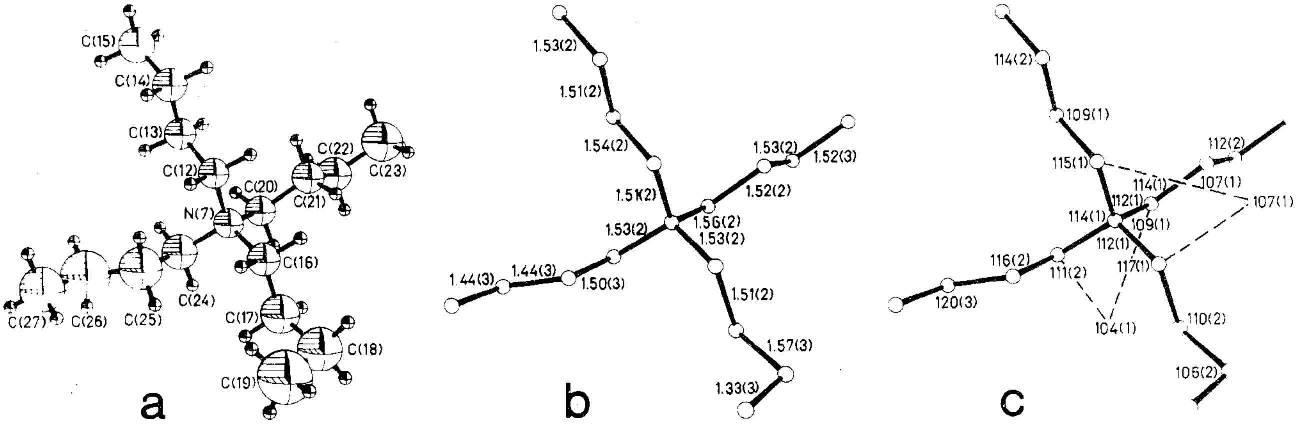


Figure 2. Labeling and dimensions of the $(n\text{-}C_4H_9)_4N^+$ ion. Hydrogen atoms are not labeled and are represented as spheres with 0.1-Å radii. Part a shows the isotropic vibration of the C and N atoms and the atomic labeling. Parts b and c show bond lengths (Å) and bond angles (degrees), respectively. Estimated standard deviations are in parentheses.

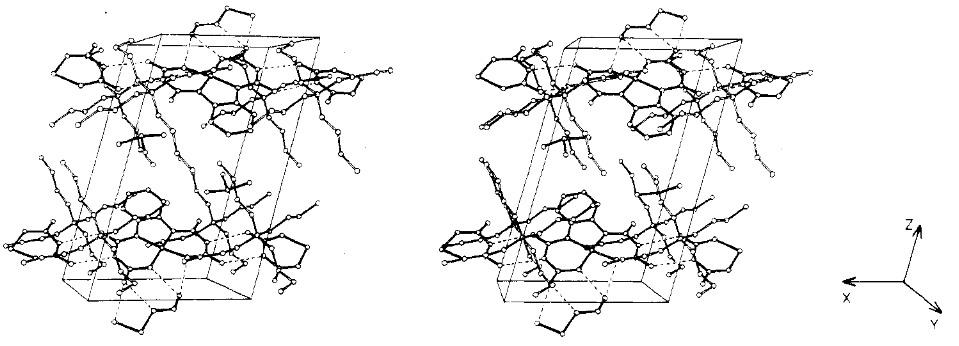


Figure 3. Stereoplot of the unit cell of $(n\text{-}C_4H_9)_4N^+Cu[o\text{-phen(bi)}_2]\cdot CHCl_3$. Hydrogen bonds are indicated with dashed lines.

with deprotonated biuret. The copper atom is surrounded by an approximately planar arrangement of four nitrogen atoms. The Cu–N distances are short: 1.82 (1), 1.85 (1), 1.86 (1), and 1.89 (1) Å (see Discussion).

The distances of the Cu, N(1), N(2), N(4), and N(5) atoms from a least-squares plane fitted to these atoms are −0.003 (2), 0.14 (1), 0.10 (1), 0.11 (1), and 0.12 (1) Å, respectively. In the axial direction the atoms closest to the Cu atom are two carbon atoms of the $(n\text{-}C_4H_9)_4N^+$ ions: Cu–C(22) = 3.75 (2) Å, Cu–C(18) = 3.84 (2) Å (see Figure 3).

There are four hydrogen bonds between each complex ion and a complex symmetry related to it by inversion [see in Figure 1: O(3)···N(1′), O(3)···N(4′), N(4)···O(3′), N(1)···O(3′)]. Two additional hydrogen bonds are formed between each pair of complex ions related by a unit cell translation in the x direction [see in Figure 1: N(3)···O(4″), O(1)···N(6″)]. The resulting layers of (hydrogen-bonded) complex anions and the chloroform molecules are embedded between the n-butyl chains of the $(n\text{-}C_4H_9)_4N^+$ ions.

The high temperature factors for some C atoms in the $(n\text{-}C_4H_9)_4N^+$ ion indicate extensive thermal motion or a slight disorder in their positions. It offers an explanation for the fact that reflections with $\theta > 20°$ were unobservably weak (resolution of data is 1 Å).

Disorder in the orientation of the butyl chains may also be the reason that the apparent bond length of one of the C–C bonds in the $(n\text{-}C_4H_9)_4N^+$ ion is shorter than would be expected [C(18)–C(19) = 1.33 (3) Å].

Discussion

Coordination Geometry in Complexes of Deprotonated Biuret. The stabilization of high oxidation states in complexes in which the central metal atom is coordinated by deprotonated amide groups is now well established. The synthesis and characterization of Co^{III}, Cu^{III}, and Ni^{III} complexes with biuret and substituted biuret ligands were reported earlier.[1-3] It was postulated that the strong electron donation by the deprotonated amide nitrogen atoms results in a relatively high electron density on the central metal atom.[2,3] This facilitates oxidation of the metal center, reduces the electrophilicity of the metal atom, and results in a preference for planar four-coordination. This coordination geometry is invariably found in Cu^{II}, Cu^{III}, Ni^{II}, and Ni^{III} complexes of deprotonated biuret[1-3,5-7,19] and is favored in Co^{III} complexes of deprotonated biuret.[6,7] However, thermally unstable diamagnetic six-coordinated bis(amino)bis(biuretato)cobaltate(III) complexes can be prepared.[3]

Table I. Atomic Positional and Thermal Parameters for $(n\text{-}C_4H_9)_4NCu[o\text{-phen(bi)}_2]\cdot CHCl_3$[a]

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cu	4487(2)	2810(2)	1484(1)	16(1)	47(1)	56(1)	5(1)	14(1)	23(1)
Cl(1)	2635(6)	3469(6)	3824(4)	74(4)	146(6)	159(6)	−28(4)	51(4)	−34(5)
Cl(2)	1310(7)	1435(6)	4485(4)	163(6)	131(6)	105(5)	56(5)	35(4)	55(4)
Cl(3)	−18(7)	3681(6)	4208(5)	120(5)	106(5)	212(4)	39(4)	101(5)	32(5)

Atom	10^3x	10^3y	10^3z	10^3U_{iso}	Atom	10^3x	10^3y	10^3z	10^3U_{iso}
N(1)	282(1)	360(1)	116(1)	46(3)	C(9)	731(1)	69(1)	300(1)	39(4)
N(2)	374(1)	173(1)	213(1)	36(3)	C(10)	621(1)	133(1)	255(1)	33(4)
N(3)	134(1)	224(1)	167(1)	40(3)	C(11)	104(2)	266(2)	387(1)	67(5)
N(4)	515(1)	373(1)	76(1)	44(3)	C(12)	69(2)	795(1)	309(1)	59(5)
N(5)	627(1)	218(1)	194(1)	35(3)	C(13)	157(2)	705(2)	365(1)	66(5)
N(6)	757(1)	334(1)	117(1)	38(3)	C(14)	238(2)	777(2)	447(1)	76(5)
N(7)	−22(1)	736(1)	225(1)	58(4)	C(15)	335(2)	697(2)	508(1)	87(6)
O(1)	45(1)	382(1)	93(1)	61(4)	C(16)	−103(2)	839(2)	180(1)	67(5)
O(2)	184(1)	66(1)	248(1)	53(3)	C(17)	−195(2)	805(2)	92(1)	95(6)
O(3)	687(1)	479(1)	27(1)	54(3)	C(18)	−272(2)	921(2)	57(1)	113(7)
O(4)	865(1)	203(1)	206(1)	61(3)	C(19)	−178(3)	988(3)	27(2)	116(11)
C(1)	149(2)	324(1)	124(1)	47(4)	C(20)	−133(2)	628(1)	235(1)	63(5)
C(2)	231(1)	151(1)	211(1)	43(4)	C(21)	224(2)	664(2)	292(1)	70(5)
C(3)	653(1)	400(1)	71(1)	40(4)	C(22)	−333(2)	552(2)	209(1)	84(6)
C(4)	750(1)	250(1)	173(1)	41(4)	C(23)	−429(2)	577(2)	346(1)	117(8)
C(5)	480(1)	111(1)	267(1)	34(4)	C(24)	66(2)	673(2)	173(1)	84(6)
C(6)	460(1)	39(1)	330(1)	49(4)	C(25)	179(3)	765(2)	158(1)	118(8)
C(7)	574(2)	−21(1)	377(1)	53(4)	C(26)	303(3)	713(3)	141(2)	161(11)
C(8)	709(1)	−6(1)	361(1)	49(4)	C(27)	421(3)	795(2)	129(2)	128(9)

[a] Standard deviations are given in parentheses. Temperature factors are of the forms $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ and $\exp[-8\pi^2U_{iso}((\sin\theta)/\lambda)^2]$.

Comparison with Copper Peptide Complexes. In Cu complexes with deprotonated peptides the Cu atom is bound

Table II. Polarographic Data for One-Electron Reduction of Some Cu^{III} and Co^{III} Biuret Complexes[a]

Complex	$E_{1/2}$, V	$\lvert E_{3/4} - E_{1/4} \rvert$,[b] mV	Ref
$(n\text{-}C_4H_9)_4NCu[o\text{-phen(bi)}_2]\cdot CHCl_3$	0.04	75	*c*
$KCu[3\text{-Pr(bi)}]_2\cdot 2H_2O$[d]	−0.36	61	2
$(n\text{-}C_4H_9)_4NCo[o\text{-phen(bi)}_2]\cdot CHCl_3$	−0.47	60	3
$KCo[3\text{-Pr(bi)}]_2\cdot 2H_2O$	−0.71	60	3

[a] More data are given in ref 2 and 3. [b] The theoretical value for a reversible *n*-electron process is $(RT/nF)\ln 9$ (56 mV at 25 °C for $n = 1$). [c] See Experimental Section. [d] 3-Pr(bi) = $(HNCON(C_3H_7)CONH)^{2-}$.

to the terminal NH_2 group and not more than three deprotonated amide groups.[19] For a series of copper(II) peptide complexes it has been shown that there is a decreasing interaction with axial ligands as the number of coordinated N atoms increases.[19] This illustrates the good electron-donor properties of deprotonated peptide ligands.

The existence of $Cu^{III}(bi)_2^-$ and $Co^{III}(bi)_2^-$ and the nonexistence of $Cu^{III}(en)_2^{3+}$ and $Co^{III}(en)_2^{3+}$ show that deprotonated amide nitrogen atoms are stronger electron donors than amino nitrogen atoms. The number of deprotonated amide groups around the central metal atom is smaller (≤ 3) in complexes of peptides than in complexes of biuret (4) and the electron-donor capacity of the ligand as a whole is therefore smaller in the peptide complexes. The oxidation of peptide complexes is consequently more difficult. For instance, $Cu^{II}[o\text{-phen(bi)}_2]^{2-}$ and $Cu^{II}(bi)_2^{2-}$ can be oxidized with I_2, but copper(III) triglycylglycine oxidizes I^-.[11] For the oxidation of copper(II) triglycylglycine stronger oxidizing agents such as $IrCl_6^{2-}$ are necessary. Similarly the presence of an electron-withdrawing substituent on a deprotonated amide group (such as the phenylene group in the present compound) increases the oxidation potential (Table II).

Planar Four-Coordination and Unusual Spin States. Planar four-coordinated Co^{III} complexes are known with different sets of donor atoms: N_4 (biuret),[3,6,7] S_4 (dithiols),[20] S_2N_2 (*o*-aminothiophenol),[21] and S_2O_2 (*o*-mercaptophenol).[22] All these complexes are spin triplets at room temperature. For the N_4- and S_4-coordinated Co^{III} complexes it has been shown that $S = 1$ is the spin ground state.[3,23]

In planar four-coordinated complexes a single d orbital points directly toward the ligands. Extended Hückel molecular orbital (EHMO) calculations for $Co(bi)_2^-$ showed[3] that this orbital has a much higher energy than the remaining four d orbitals as ligand field theory predicts. The six d electrons in Co^{III} complexes are distributed in a high-spin way over the four low-energy d orbitals. This results in a spin triplet state irrespective of the relative ordering of these four d-orbital levels. Similar arguments explain (i) the paramagnetism ($S = 1$) of square-pyramidal five-coordinated Co^{III} complexes with a weak axial ligand[24,25] (donor atoms N_4X, where X = Cl, Br, or I), (ii) the unusual spin ground states observed for manganese(II) phthalocyanine[26] (planar N_4 coordination; d^5; $S = {}^3/_2$) and iron(II) phthalocyanine[27] (d^6; $S = 1$), and (iii) the diamagnetism of the copper(III) biuret complexes[2] (d^8; $S = 0$) and the paramagnetism of nickel(III) biuret complexes[2] (d^7; $S = {}^1/_2$).

The Reality of High Metal Oxidation States. There are several reasons why the oxidized complexes of biuret and peptides should be described as complexes of tervalent metals.

(i) Molecular orbital calculations for $Co(bi)_2^-$ have shown[3] that there is little mixing of d orbitals with ligand orbitals. Presumably the energy difference between the cobalt d orbitals and the nitrogen s and p orbitals is too large. The same is true for the energies of the d orbitals of copper and nickel.[28] Thus the highest filled and first empty molecular orbitals have almost pure metal d character. Redox reactions which involve these orbitals must therefore take place on the metal.

Table III. Comparison of Cu^{II}–N, Cu^{III}–N and Ni^{II}–N Bond Lengths in Planar Peptide and Biuret Complexes (Å) (Standard Deviations in Parentheses)

Complex	*d*(M–N)[a]	Ref	Complex	*d*(M–N)[a]	Ref
$Na_2Cu(H_{-3}GGGG)\cdot 10H_2O$[b]	1.923 (4)	29	Present Cu^{III} complex	1.82 (1)	
	1.912 (4)			1.85 (1)	
	1.944 (4)			1.86 (1)	
$K_2Cu(bi)_2\cdot 4H_2O$	1.93 (1)	5		1.89 (1)	
	1.93 (2)		$Na_2Ni(H_{-3}GGGG)\cdot 8H_2O$	1.83 (1)	30
				1.84 (1)	
				1.87 (1)	

[a] *d*(M–N) = metal–N(deprotonated amide) bond length. [b] Disodium triglycylglycinatocuprate(II) decahydrate.

(ii) For a series of four-coordinated Co^{III} complexes (including two complexes of biuret with different substituents) there is a parallel behavior in increasing redox potential for the Co^{III}–Co^{II} couple (as indicated by polarographic half-wave potentials) and increasing electrophilicity of the central metal atom (a greater affinity for further ligands and a tendency to form dimers in which the metal is five-coordinated).[21] Apparently the oxidation potential is dependent on the electronic charge on the metal, showing that redox processes take (at least partly) place at the central metal atom. Oxidation of complexes of divalent metals with these ligands must therefore result in a higher oxidation state of the metal.

(iii) Oxidation of Cu^{II} (d^9) in a square-planar ligand field involves removal of one electron from the antibonding $d_{x^2-y^2}$ orbital and the Cu^{III} complex thus obtained is isoelectronic with a Ni^{II} complex of the same ligand. Some properties of planar Cu^{III} and Ni^{II} biuret and peptide complexes are similar. They are all diamagnetic and it has been observed that both Ni^{II} and Cu^{III} peptide complexes are sluggish in their substitution reactions.[11] In contrast substitution reactions in complexes of the parent Cu^{II} complexes are fast. The present structure shows additional similarity between Ni^{II} and Cu^{III} complexes. The Ni^{II}–N(deprotonated amide) bond lengths found in a planar Ni^{II} peptide complex are significantly shorter than those found in the corresponding Cu^{II} complex in which the antibonding $d_{x^2-y^2}$ orbital is half-filled (See Table III). The Ni^{II}–N(deprotonated amide) bond lengths are close to the Cu^{III}–N distances in the present structure.

Conclusion

It has been suggested that Cu^{III} plays a role in the redox reactions of some Cu-containing enzymes such as galactose oxidase[31,32] and tyrosinase.[32] The present structure and related work on Cu^{III} peptide complexes[11] show that there is a possibility that biologically important molecules may provide donor groups and coordination geometries which stabilize high oxidation states.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and of the parameters used in calculating the hydrogen atom contributions to the F_c (20 pages). Ordering information is given on any current masthead page.

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Polybismuth Anions. Synthesis and Crystal Structure of a Salt of the Tetrabismuthide(2−) Ion, Bi_4^{2-}. A Basis for the Interpretation of the Structure of Some Complex Intermetallic Phases[1]

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The intermetallic compounds K_5Bi_4 and K_3Bi_2 have been found to react with solutions of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt) in ethylenediamine to form deep green–red dichroic solutions. These spontaneously deposit black crystals of the compound 2,2,2-crypt–potassium tetrabismuthide(2−), $(C_{18}H_{36}N_2O_6K^+)_2Bi_4^{2-}$, with more reduced compounds remaining in solution. This compound crystallizes in the triclinic space group $P\bar{1}$ with lattice constants a = 11.604 (4) Å, b = 11.796 (4) Å, c = 11.096 (3) Å, α = 98.12 (3)°, β = 98.02 (3)°, and γ = 61.37 (3)° with one formula unit per cell. Three-dimensional x-ray data were collected from two crystals on an automated diffractometer using monochromatic Mo Kα radiation, and the structure was deduced by conventional heavy atom techniques. Positional and anisotropic thermal parameters of the 29 independent nonhydrogen atoms refined by full matrix least squares using 2704 unique observed ($I > 3\sigma_I$) reflections to R = 0.121, R_w = 0.147. Four of the carbon atoms in the ligand exhibit extremely anisotropic thermal parameters, which effect was resolved and refined in terms of pairs of disordered atoms at 0.50 occupancy. The Bi_4^{2-} anion effectively exhibits D_{4h} symmetry with observed bond lengths of 2.936 (2) and 2.941 (2) Å and bond angles of 89.85 (6) and 90.15 (6)°. The bonding is considered to be the same as in the isoelectronic Te_4^{2+}. The Bi_4^{2-} ion provides a useful starting point for the interpretation of the square metal groups found in the isostructural $Ca_{11}Bi_{10}$, $Ca_{11}Sb_{10}$, and $Ho_{11}Ge_{10}$.

Introduction

Cationic polybismuth clusters have been known for some time, the species Bi_5^{3+}, Bi_8^{2+}, and Bi_9^{5+} having been identified and characterized in the compound $Bi_{12}Cl_{14}$ or as solid and solution products of the reduction of $BiCl_3$ with bismuth in various acidic molten salt media.[2] Considerably less is known about anionic clusters of bismuth. Zintl et al.[3,4] found evidence for the existence of three polybismuthides, violet Bi_3^{3-} and brown Bi_5^{3-} by potentiometric titration in liquid ammonia of a solution of sodium with BiI_3 and yellow-brown Bi_7^{3-} through exhaustive extraction of bismuth-rich (Na:Bi = 1:3) alloys for a period of months. All solids recovered consisted of mixtures of NaBi and Bi.

As was recently noted,[5] the identification of the last species as Bi_7^{3-} appears questionable. The conclusion was based on the analytical result $Na_3Bi_{5.85}$ (or approximately Na_3Bi_6) which was presumed to indicate the existence of Na_3Bi_7 in solution on the grounds that no other group 5 anion had been observed