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# Square-Planar Complexes of Copper(II), Nickel(II), and Cobalt(II) with Deprotonated Biuret Derivatives. Crystalline and Molecular Structures of Sodium (*o*-Phenylenebis(biuretato))- and (Propylenebis(biuretato))cuprate(II)–Dimethyl Sulfoxide Complexes

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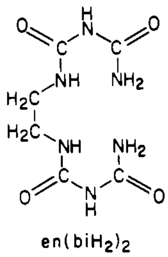
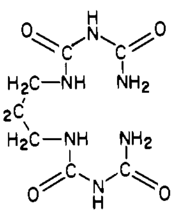
Copper(II), cobalt(II), and nickel(II) complexes of the anionic *o*-phenylenebis(biuretato) ligand have been prepared. With ethylene- and propylenebis(biuret) only the copper and nickel complexes have been isolated. The structures of two compounds have been determined by X-ray analysis. Compound a, $Na_2Cu(o\text{-}C_6H_4(NCONHCONH)_2)\cdot 4(OS(CH_3)_2)$, crystallizes in the $P\bar{1}$ space group with cell parameters $a = 9.753$ (10) Å, $b = 16.513$ (8) Å, $c = 9.588$ (3) Å, $\alpha = 106.98$ (5)°, $\beta = 93.24$ (4)°, $\gamma = 86.21$ (4)°, $V = 1472$ (3) Å$^3$, and $Z = 2$. Compound b, $Na_2Cu(CH_2(CHNCONHCONH)_2)\cdot 3(OS(CH_3)_2)$, crystallizes in the $P2_1/c$ space group with $a = 8.198$ (16) Å, $b = 13.718$ (17) Å, $c = 21.58$ (6) Å, $\beta = 98.63$ (10)°, $V = 2400$ (9) Å$^3$, and $Z = 4$. Compound a shows a square-planar coordination around the copper atom with four deprotonated nitrogen atoms, whereas compound b presents a distorted four-coordination with a flattened tetrahedron. The $Cu^{II}$–N bond lengths are in the range 1.909–1.964 Å for compound a and 1.928–1.987 Å for compound b; they are larger than the $Cu^{III}$–N distances in a related complex and are in good agreement with $Cu^{II}$–N(peptide) distances. The sodium ions are surrounded by oxygen atoms. The corresponding cobalt(II) and nickel(II) complexes are isostructural with compound a. The electronic spectra are consistent with the geometry found around the metal. Oxidation reactions are reported.

## Introduction

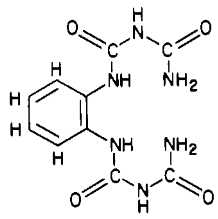
Deprotonated polypeptide copper and nickel complexes are well described in the literature.[2-4] These compounds involve the redox system M(III)/M(II) which seems to play a role in biological chemistry, especially in Cu(III)/Cu(II) systems. We report here the synthesis and the properties of Cu(II), Ni(II), and Co(II) complexes with ligands coordinated via deprotonated amide groups. The synthesized ligands are biuret ($biH_2$) derivatives bonded with the following bridging groups: *o*-phenylene (ophen), ethylene (en), and propylene (pr).



en(biH$_2$)$_2$



pr(biH$_2$)$_2$



ophen(biH$_2$)$_2$

The influence of this bridging group on the metal ion geometry has been studied in order to relate it with the oxidizability of the complexes. Compounds with *o*-phenylenebis(biuret) and ethylenebis(biuret) ligands have been described previously: Cu(III)[5] and Co(III)[6] compounds show a square-planar coordination geometry. We note also that XPS spectra have been reported for copper complexes with these two ligands.[7]

## Experimental Section

All chemicals were reagent grade, and all preparations were performed under nitrogen.

**Preparation of the Ligands.** The three ligands were prepared according to the method described by Birker for *o*-phenylenebis(biuret),[5] which involved a condensation reaction of freshly prepared nitrobiuret[8] with diamine. They were identified by elemental analyses and $^1H$ NMR spectra (Table SI, supplementary material).

**Preparation of the Compounds.** A solution of 3 mL of sodium hydroxide (4 M) was added to a solution of ligand (3 mmol in 70 mL of dimethyl sulfoxide). Metallic perchlorate (3 mmol in 20 mL of $Me_2SO$) was very slowly added to the basic mixture. This solution, after concentration, was left standing overnight. Crystals of the complexes were filtered from the solution, washed with $Me_2SO$, and dried under vacuum. The number of the solvent crystallization molecules was determined by elemental and thermogravimetric decomposition analysis. Cobalt compounds are more reactive and are very air and solvent sensitive. Analytical data are collected in Table I.

**Physical Measurements.** Electronic spectra were recorded with a Beckman 5240 spectrophotometer. Magnetic susceptibilities were determined at room temperature (20 °C) with use of $CuSO_4\cdot 5H_2O$ as calibrant; diamagnetic susceptibility corrections were calculated from Pascal's constants.[9]

**X-ray Studies: Powder Data.** For the seven compounds, the powder data were collected with a Debye–Scherrer camera (Ni filtered; $K\alpha$ copper radiation; $\lambda = 1.5418$ Å). These compounds are well crystallized and show the following isostructural relations (Table SII, supplementary material): (A) $Na_2[Co(ophen(bi)_2)]\cdot 4Me_2SO$, $Na_2[Ni(ophen(bi)_2)]\cdot 4Me_2SO$, $Na_2[Cu(ophen(bi)_2)]\cdot 4Me_2SO$; (B) $Na_2[Ni(en(bi)_2)]\cdot 2Me_2SO$, $Na_2[Cu(en(bi)_2)]$; (C) $Na_2[Ni(pr(bi)_2)]\cdot 3Me_2SO$; (D) $Na_2[Cu(pr(bi)_2)]\cdot 3Me_2SO$.

**X-ray Structural Studies.** Among the preceding complexes, two copper complexes were sufficiently crystalline to make possible structural studies. The crystals of the compound $Na_2[Cu(ophen(bi)_2)]\cdot 4$ $Me_2SO$ are red and crystallize in two forms: thin plates and prisms. They were not very sensitive to atmospheric moisture, and the choice of a crystal was easy. The second compound, $Na_2[Cu(pr(bi)_2)]\cdot 3$ $Me_2SO$, was very moisture sensitive; the dark red crystals were sealed in capillaries under nitrogen. Among seven single crystals, only one was sufficiently stable for diffraction work.

**Data Collection and Structure Solution.** Diffraction experiments were performed at 20 °C on a CAD 4 Nonius diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The initial orientation matrix and the

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(1) (a) Université de Reims Champagne Ardenne. (b) Université de Poitiers.

(2) Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894.

(3) Bossu, F. P.; Chellappa, K. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 2195.

(4) Bossu, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 4003.

(5) Birker, P. J. M. W. L. *Inorg. Chem.* **1977**, *16*, 2478.

(6) Birker, P. J. M. W. L.; Bour, J. J.; Steggerda, J. J. *Inorg. Chem.* **1973**, *12*, 1254.

(7) Brown, D. G.; Weser, U. *Inorg. Chem.* **1980**, *19*, 264.

(8) Thiele, J.; Uhlfelder, E. *Justus Liebigs Ann. Chem.* **1898**, *303*, 93.

(9) Earnhaw, A. "Introduction to Magneto-Chemistry"; Academic Press: London, 1968.

**Table I.** Elemental Analysis and Magnetic Data

| compd (color) | calcd | | | | | found | | | | | $10^6\chi_M$, c.gsu | $\mu_{eff}$, $\mu_B$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % C | % H | % N | % M | % Na | % C | % H | % N | % M | % Na | | |
| $Na_2[Cu(ophen(bi)_2)]\cdot4Me_2SO$ (red) | 30.96 | 4.62 | 12.04 | 9.10 | 6.58 | 30.88 | 4.63 | 12.07 | 9.05 | 6.59 | 1660 | 1.97 |
| $Na_2[Cu(en(bi)_2)]$ (dark red) | 21.34 | 2.39 | 24.89 | 18.82 | 13.62 | 21.05 | 2.65 | 24.62 | 18.77 | 13.61 | 1280 | 1.73 |
| $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$ (purple) | 26.64 | 4.82 | 14.34 | 10.84 | 7.84 | 26.20 | 4.82 | 14.27 | 10.29 | 7.92 | 1840 | 2.08 |
| $Na_2[Ni(ophen(bi)_2)]\cdot4Me_2SO$ (orange-yellow) | 31.18 | 4.65 | 12.12 | 8.47 | 6.63 | 30.93 | 4.93 | 12.48 | 7.90 | 6.21 | *b* | *b* |
| $Na_2[Ni(en(bi)_2)]\cdot2Me_2SO$ (red-purple) | 24.56 | 4.12 | 17.18 | 12.00 | 9.40 | 24.38 | 4.70 | 16.67 | 12.35 | 9.65 | *b* | *b* |
| $Na_2[Ni(pr(bi)_2)]\cdot3Me_2SO$ (orange-red) | 26.86 | 4.84 | 14.46 | 10.10 | 7.91 | 26.20 | 5.24 | 14.30 | 10.15 | 8.40 | *b* | *b* |
| $Na_2[Co(ophen(bi)_2)]\cdot4Me_2SO$ (yellow) | 31.17 | 4.65 | 12.12 | 8.50 | 6.63 | 30.56 | 4.91 | 11.75 | 8.10 | 6.98 | 2340 | 2.34 |
| $Na_2[Co(en(bi)_2)]\cdot xMe_2SO$ (yellow)[c] | | | | | | | | | | | 2100[a] | 2.2[a] |

[a] Approximative values based only on cobalt analyses. [b] Diamagnetic. [c] This compound was too unstable to yield elemental analyses.

**Table II.** Summary of Crystal Data, Intensity Collection, and Structure Refinement

| | $Na_2[Cu(ophen(bi)_2)]\cdot4Me_2SO$ | $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$ |
|---|---|---|
| formula | $C_{18}H_{32}CuN_6Na_2O_8S_4$ | $C_{13}H_{28}CuN_6Na_2O_7S_3$ |
| fw | 698.27 | 586.12 |
| space group | $P\bar{1}$ | $P2_1/c$ |
| $a$, Å | 9.753 (10) | 8.198 (16) |
| $b$, Å | 16.513 (8) | 13.718 (17) |
| $c$, Å | 9.588 (3) | 21.58 (6) |
| $\alpha$, deg | 106.98 (5) | 90. |
| $\beta$, deg | 93.24 (4) | 98.63 (10) |
| $\gamma$, deg | 86.21 (4) | 90. |
| $V$, Å$^3$ | 1472 (3) | 2400 (9) |
| $Z$ | 2 | 4 |
| $d_{measd}$ ($d_{calcd}$), g/cm$^3$ | 1.59 (1.577) | 1.62 (1.616) |
| cryst size, mm | 0.3 × 0.28 × 0.1 | 0.6 × 0.2 × 0.2 |
| cryst faces, (hkl) | (001), (100), (010) | (100), (011), $(01\bar{1})$ |
| $\mu$, cm$^{-1}$ | 10.6 | 12.1 |
| scan method | $\omega$ | $\omega/2\theta$ |
| data collcn range ($2\theta$), deg | 6–78 | 4–52 |
| index range | $h,\pm k,\pm l$ | $\pm h,k,l$ |
| scan time, s | 50 | 60 |
| scan angle, deg | $1 + 0.35 \tan\theta$ | $2 + 0.35 \tan\theta$ |
| takeoff angle, deg | 2.5 (3 reflcns) | 4.5 (5 reflcns) |
| no. of unique data | 5047 | 4992 |
| no. of data with $I > 2\sigma(I)$ | 3469 | 2880 |
| $R$, $R_w$[a] | 0.049, 0.059 | 0.041, 0.056 |
| largest peak, e/Å$^3$ | 0.45 | 0.70 |
| largest hole, e/Å$^3$ | −0.53 | −0.50 |

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

lattice parameters were obtained from 15 machine-centered reflections chosen in the whole reciprocal space. Crystal data and data collection parameters are summarized in Table II. Three standard reflections were recorded every 97 reflections; their intensities showed no statistically significant change over the duration of data collection. The data were processed with use of the SHELX-76 program package at the computing center CIRCE (University of Orsay, Orsay, France). The scattering factors for the neutral atoms H, C, N, O, and S and the $Cu^{2+}$ and $Na^+$ ions (with anomalous dispersion) were used.[10] After the reduction program, the Cu atom position was located from a Patterson map, and the remaining non-hydrogen atoms were located from successive difference Fourier maps. The last calculation permits the location of the hydrogen atoms in the complex anion. Positions of the hydrogens of the solvent molecules were calculated with the C–H bond length fixed at 1.08 Å. All these hydrogen atoms were included but not refined for the final full-matrix refinement cycles. The last difference Fourier map showed no peaks of chemical significance, the largest peaks being in the vicinity of the copper atom. Final $R$ factors are included in Table II. The weighting scheme was first $w = 1$ and then $K/\sigma^2(F_o)$. No absorption corrections were made because of the absorption coefficient being low. Azimuthal scans for 10 reflections showed a maximum intensity deviation of 4%.

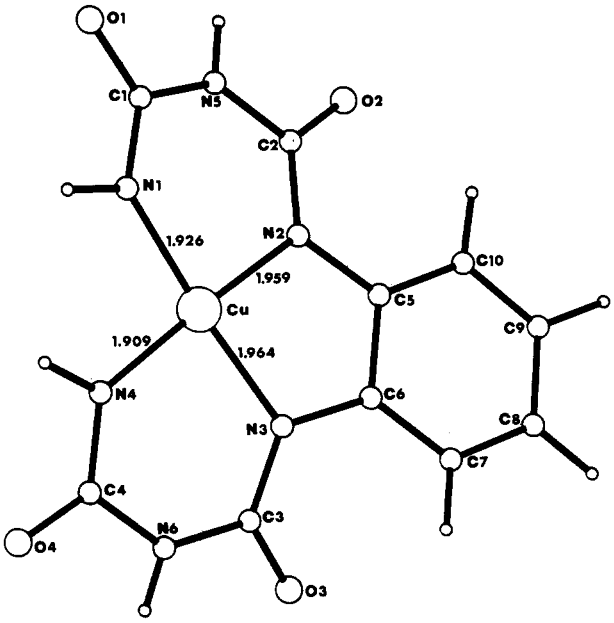

**Figure 1.** Drawing of the complex anion $[Cu(ophen(bi)_2)]^{2-}$.

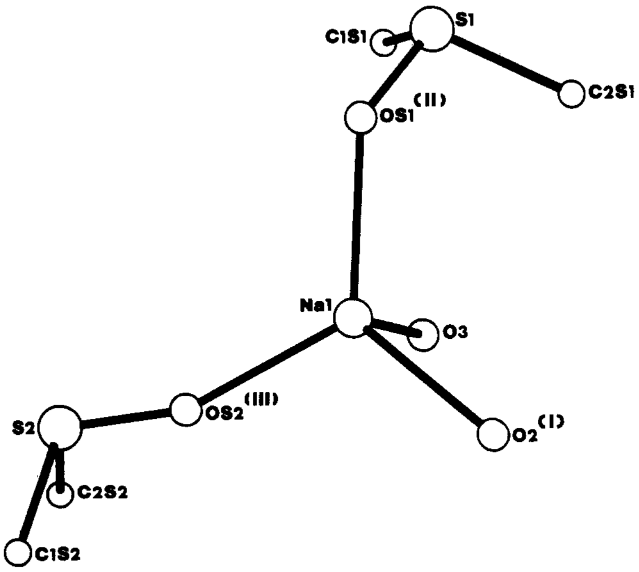

**Figure 2.** Coordination around sodium cation Na1 in $Na_2[Cu(ophen(bi)_2)]\cdot4Me_2SO$.

## Results and Discussion

**Crystal Structure of $Na_2[Cu(ophen(bi)_2)]\cdot4Me_2SO$.** The following results are tabulated: positional parameters (Table III) and interatomic distances and angles (Table IV). Figure 1[11] represents the $[Cu(ophen(bi)_2)]^{2-}$ complex anion with the copper atoms lying between four nitrogen atoms. The coordination around the copper atom is practically planar ($\sum$(angles) = 360.3°), the

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(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55, 150.

(11) The drawings were computed with a personal (C.K.) drawing program on a PDP-11 computer.

**Table III.** Positional Parameters and Their Estimated Standard Deviations for $Na_2[Cu(ophen(bi)_2)]\cdot 4Me_2SO$

| atom | $x$ | $y$ | $z$ | $B_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Cu | 0.12341 (6) | 0.30662 (4) | 0.09831 (7) | 2.2 |
| O1 | −0.2681 (3) | 0.3497 (2) | 0.2541 (4) | 3.5 |
| O2 | −0.1590 (3) | 0.1323 (2) | −0.1225 (4) | 3.3 |
| O3 | 0.5138 (3) | 0.2166 (2) | −0.0311 (4) | 2.9 |
| O4 | 0.4357 (3) | 0.4304 (3) | 0.3649 (4) | 3.8 |
| N1 | −0.0414 (4) | 0.3508 (3) | 0.2022 (5) | 3.0 |
| N2 | 0.0244 (4) | 0.2201 (2) | −0.0500 (4) | 2.2 |
| N3 | 0.2823 (4) | 0.2604 (2) | −0.0226 (4) | 2.1 |
| N4 | 0.2338 (4) | 0.3821 (3) | 0.2435 (5) | 3.6 |
| N5 | −0.1831 (4) | 0.2446 (3) | 0.0722 (5) | 3.1 |
| N6 | 0.4480 (4) | 0.3276 (3) | 0.1533 (4) | 2.6 |
| C1 | −0.1636 (5) | 0.3189 (3) | 0.1817 (5) | 2.8 |
| C2 | −0.1033 (5) | 0.1957 (3) | −0.0410 (6) | 2.6 |
| C3 | 0.4144 (5) | 0.2645 (3) | 0.0264 (5) | 2.3 |
| C4 | 0.3696 (5) | 0.3833 (3) | 0.2608 (6) | 3.0 |
| C5 | 0.1053 (4) | 0.1771 (3) | −0.1708 (5) | 2.1 |
| C6 | 0.2449 (4) | 0.2011 (3) | −0.1556 (5) | 2.1 |
| C7 | 0.3282 (5) | 0.1691 (3) | −0.2747 (5) | 2.6 |
| C8 | 0.2823 (5) | 0.1106 (4) | −0.4011 (5) | 3.2 |
| C9 | 0.1488 (5) | 0.0847 (3) | −0.4122 (5) | 3.2 |
| C10 | 0.0614 (5) | 0.1192 (3) | −0.2989 (5) | 2.8 |
| Na1 | 0.6199 (2) | 0.1081 (1) | −0.2090 (2) | 2.8 |
| Na2 | −0.3361 (2) | 0.4515 (1) | 0.4586 (2) | 3.3 |
| S1 | 0.2964 (2) | 0.0766 (1) | 0.1157 (2) | 5.0 |
| OS1 | 0.3829 (4) | 0.0280 (3) | 0.2026 (5) | 5.0 |
| C1S1 | 0.1275 (8) | 0.0817 (5) | 0.1791 (8) | 6.6 |
| C2S1 | 0.2729 (8) | 0.0043 (5) | −0.0611 (7) | 5.7 |
| S2 | 0.3481 (2) | 0.8753 (1) | 0.5763 (2) | 5.4 |
| OS2 | 0.3640 (5) | 0.8623 (4) | 0.4177 (5) | 7.5 |
| C1S2 | 0.4572 (7) | 0.7960 (5) | 0.6211 (9) | 6.6 |
| C2S2 | 0.1884 (7) | 0.8295 (7) | 0.5834 (10) | 8.8 |
| S31[a] | −0.3361 (5) | 0.3503 (3) | 0.7677 (5) | 8.1 |
| S32[b] | −0.3384 (7) | 0.4296 (4) | 0.7893 (6) | 7.6 |
| OS3 | −0.2798 (6) | 0.3825 (4) | 0.6404 (6) | 8.4 |
| C1S3 | −0.5023 (14) | 0.3886 (9) | 0.7657 (13) | 13.9 |
| C2S3[a] | −0.2805 (24) | 0.4393 (17) | 0.9310 (18) | 11.4 |
| C3S3[b] | −0.2764 (41) | 0.3543 (29) | 0.8791 (32) | 16.3 |
| S41[a] | −0.0581 (4) | 0.5916 (3) | 0.3950 (5) | 6.7 |
| S42[b] | −0.1784 (5) | 0.6046 (3) | 0.3597 (6) | 7.0 |
| OS4 | −0.1564 (5) | 0.5352 (3) | 0.4235 (6) | 6.6 |
| C1S4 | −0.0998 (14) | 0.6927 (6) | 0.4648 (11) | 12.0 |
| C2S4 | −0.0797 (14) | 0.5887 (8) | 0.2114 (13) | 13.2 |

[a] Site occupation factor 0.6. [b] Site occupation factor 0.4.

slight tetrahedral distortion being probably due to the steric constraints of the ligand.[12] The anion is almost planar. The dihedral angle between the benzene ring and the $CuN_4$ group equals 10.8°.

The coordination around the sodium cations is respectively tetrahedral for Na1 (Figure 2) and nearly trigonal bipyramidal for Na2 (Figure 3). The solvent molecules are only bonded to the sodium cations through the oxygen atom. Two $Me_2SO$ molecules are partially disordered, and an occupation factor was first refined and then fixed. The sulfur atom of the third $Me_2SO$ molecule is disordered over two positions, S31 and S32. Among the atoms bonded to this sulfur atom, only one methyl group is also disordered with the same occupation factor. For the fourth solvent molecule only the sulfur atom shows the same disorder (S41 and S42), giving two pyramidal configurations with the sulfur atom lying over or under the plane of the three other atoms: OS4, C1S4, C2S4 (see Figure 3).

Figure 4 represents the packing of this compound with the linkages between oxygen and sodium atoms. Each complex anion is bonded to five sodium cations, forming double chains along the $\vec{a}$ axis. The cohesion of the double chain is due to the two close Na2 sodium cations, which are related by the inversion center. These two cations are bonded to four complex anions, thus forming four-membered cyclic linkages, as can be seen in the middle of the cell. Each Na1 sodium cation is bonded to two anions, linking the outer part of the double chain. These double chains are approximately flat, parallel to the (011) plane, with the solvent molecules lying over and under the chains.

**Table IV.** Principal Bond Distances (Å) and Bond Angles (deg) for $Na_2[Cu(ophen(bi)_2)]\cdot 4Me_2SO$

| | | | |
|---|---|---|---|
| (a) Coordination in Complex Anion | | | |
| Cu-N1 | 1.926 (4) | Cu-N3 | 1.964 (4) |
| Cu-N2 | 1.959 (3) | Cu-N4 | 1.909 (4) |
| N1-C1 | 1.317 (6) | C2-O2 | 1.246 (6) |
| C1-O1 | 1.259 (6) | C2-N2 | 1.348 (6) |
| C1-N5 | 1.378 (6) | N2-C5 | 1.420 (6) |
| N5-C2 | 1.391 (6) | | |
| C5-C10 | 1.384 (6) | C9-C8 | 1.385 (8) |
| C5-C6 | 1.430 (6) | C8-C7 | 1.384 (6) |
| C10-C9 | 1.382 (7) | C7-C6 | 1.393 (6) |
| C6-N3 | 1.409 (5) | N6-C4 | 1.391 (6) |
| N3-C3 | 1.345 (6) | C4-O4 | 1.248 (6) |
| C3-O3 | 1.254 (5) | C4-N4 | 1.326 (6) |
| C3-N6 | 1.391 (5) | | |
| N1-Cu-N2 | 92.4 (2) | N4-Cu-N1 | 91.7 (2) |
| N2-Cu-N3 | 84.0 (1) | N1-Cu-N3 | 175.3 (2) |
| N3-Cu-N4 | 92.2 (2) | N2-Cu-N4 | 174.2 (2) |
| (b) Coordination around Sodium Cations | | | |
| N1-O2$^{I}$ | 2.284 (4) | Na1-OS1$^{II}$ | 2.269 (5) |
| Na1-O3 | 2.315 (3) | Na1-OS2$^{III}$ | 2.209 (5) |
| Na2-O1 | 2.276 (4) | Na2-OS3 | 2.369 (6) |
| Na2-O4$^{IV}$ | 2.361 (4) | Na2-OS4 | 2.399 (5) |
| Na2-O4$^{V}$ | 2.370 (4) | | |

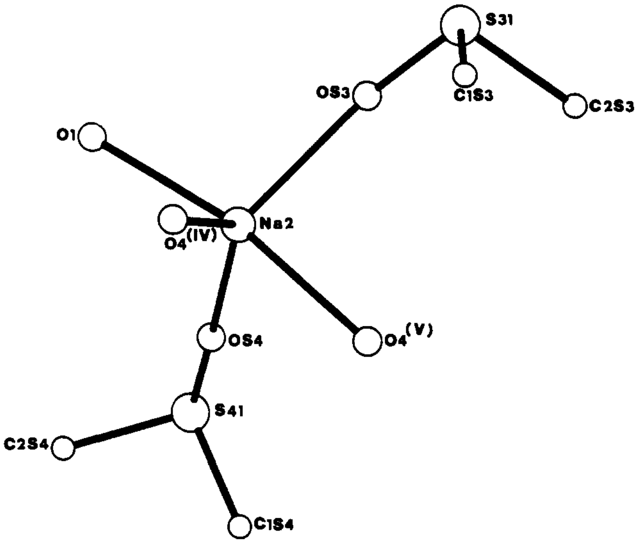

**Figure 3.** Coordination around sodium cation Na2 in $Na_2[Cu(ophen(bi)_2)]\cdot 4Me_2SO$. The disordered atoms with the highest site occupation factors are represented.

**Crystal Structure of $Na_2[Cu(pr(bi)_2)]\cdot 3Me_2SO$.** The positional parameters (Table V) and interatomic distances and angles (Table VI) are given. Figure 5 presents the complex anion $[Cu(pr(bi)_2)]^{2-}$. The coordination geometry of the copper atom shows a markedly tetrahedral distortion, the copper environment being rather a flattened tetrahedron. The solvent molecules are not coordinated to the copper atom. The question of the origin of this distortion (ligand constraints or crystal packing) remains open. Another example of a flattened, pseudotetrahedral $CuN_4$ environment with the monodentate ligand cyclohexylamine was recently published.[13] Since it was not our purpose to investigate such distortions, no further studies were made. This structural feature can possibly be related with the difficulty to prepare this compound and with its sensitivity as compared to the preceding one. Among the three solvent molecules, one is disordered over

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(12) The highest deviation from the mean plane $CuN_4$ is 0.064 Å.

(13) Gouteron, J.; Jeannin, S.; Jeannin, Y.; Livage, J.; Sanchez, C. *Inorg. Chem.* **1984**, *23*, 3387.

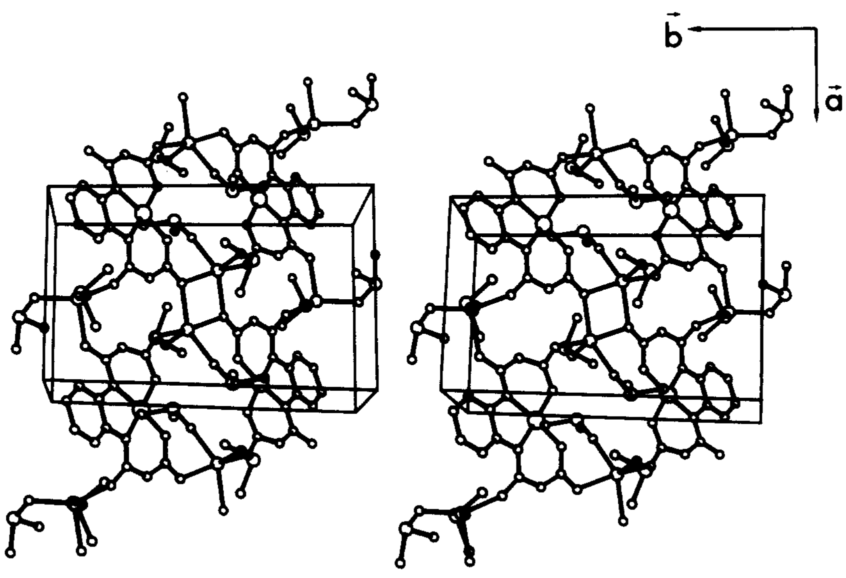

**Figure 4.** Stereoview of the cell contents for $Na_2[Cu(ophen(bi)_2)]\cdot4Me_2SO$.

**Table V.** Positional Parameters for $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$

| atom | *x* | *y* | *z* | $B_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Cu | 0.19564 (7) | 0.32019 (4) | 0.86064 (2) | 2.2 |
| O1 | 0.1779 (4) | 0.3765 (2) | 0.6748 (1) | 3.0 |
| O2 | −0.0188 (4) | 0.5841 (2) | 0.8049 (2) | 3.2 |
| O3 | 0.1860 (4) | 0.2075 (2) | 1.0390 (1) | 3.0 |
| O4 | 0.1421 (5) | 0.0213 (2) | 0.8700 (2) | 3.0 |
| N1 | 0.2573 (5) | 0.3369 (3) | 0.7776 (2) | 2.5 |
| N2 | 0.1182 (5) | 0.4558 (3) | 0.8578 (2) | 2.5 |
| N3 | 0.2145 (5) | 0.3008 (3) | 0.9527 (2) | 2.8 |
| N4 | 0.1756 (6) | 0.1818 (3) | 0.8459 (2) | 3.7 |
| N5 | 0.0813 (5) | 0.4676 (3) | 0.7482 (2) | 2.5 |
| N6 | 0.1971 (6) | 0.1294 (3) | 0.9483 (2) | 3.0 |
| C1 | 0.1760 (6) | 0.3902 (3) | 0.7323 (2) | 2.2 |
| C2 | 0.0599 (6) | 0.5051 (3) | 0.8073 (2) | 2.5 |
| C3 | 0.1990 (6) | 0.2170 (3) | 0.9817 (2) | 2.4 |
| C4 | 0.1698 (6) | 0.1093 (3) | 0.8851 (2) | 2.5 |
| C5 | 0.2216 (9) | 0.3818 (4) | 0.9973 (2) | 4.3 |
| C6 | 0.2431 (8) | 0.4803 (4) | 0.9670 (3) | 4.0 |
| C7 | 0.1050 (8) | 0.5063 (4) | 0.9164 (2) | 3.6 |
| Na1 | −0.0123 (2) | −0.0868 (1) | 0.9217 (1) | 2.8 |
| Na2 | −0.1393 (3) | 0.7129 (1) | 0.8635 (1) | 2.9 |
| S1 | 0.4890 (2) | 0.0662 (1) | 0.6998 (1) | 4.9 |
| OS1 | 0.3926 (6) | 0.1592 (3) | 0.6851 (3) | 6.3 |
| C1S1 | 0.4076 (14) | −0.0162 (8) | 0.6439 (4) | 9.9 |
| C2S1 | 0.4062 (14) | 0.0111 (8) | 0.7614 (5) | 10.4 |
| S2 | 0.2812 (2) | 0.7417 (1) | 0.8668 (1) | 4.1 |
| OS2 | 0.1371 (5) | 0.7683 (3) | 0.8992 (2) | 4.1 |
| C1S2 | 0.2212 (9) | 0.7724 (5) | 0.7867 (3) | 5.4 |
| C2S2 | 0.4294 (8) | 0.8356 (5) | 0.8853 (4) | 5.4 |
| S31[a] | 0.6981 (5) | 0.1156 (3) | 0.9472 (2) | 6.2 |
| S32[b] | 0.7507 (9) | 0.1086 (5) | 0.9190 (3) | 6.0 |
| OS3 | 0.8489 (5) | 0.0541 (3) | 0.9724 (2) | 4.1 |
| C1S3 | 0.7713 (16) | 0.2366 (7) | 0.9453 (5) | 10.7 |
| C2S3[a] | 0.6904 (31) | 0.1051 (16) | 0.8639 (7) | 14.2 |
| C3S3[b] | 0.5587 (23) | 0.1028 (25) | 0.9317 (15) | 10.8 |

[a] Site occupation factor 0.6. [b] Site occupation factor 0.4.

two positions (sulfur atom S31 and S32, methyl group C2S3 and C3S3; given in Table V, not shown in Figure 6). The oxygen atoms of the complex anion are bonded to six sodium cations; the coordination geometry for the sodium cations is octahedral for Na1 (Figure 6) and trigonal bipyramidal for Na2 (Figure 7). Figure 8 shows a view of the cell contents. The linkage feature is not the same as before, but much more complicated, the bonds between anions and cations making a three-dimensional assembly.

**Comparison with a Copper(III) Compound.** Although these two compounds do not show the same coordination geometry for the copper atom, the two biuret parts are planar and present the same features as can be seen from Table VII. We can notice that the Cu–N bond lengths are shorter for the terminal nitrogen atoms

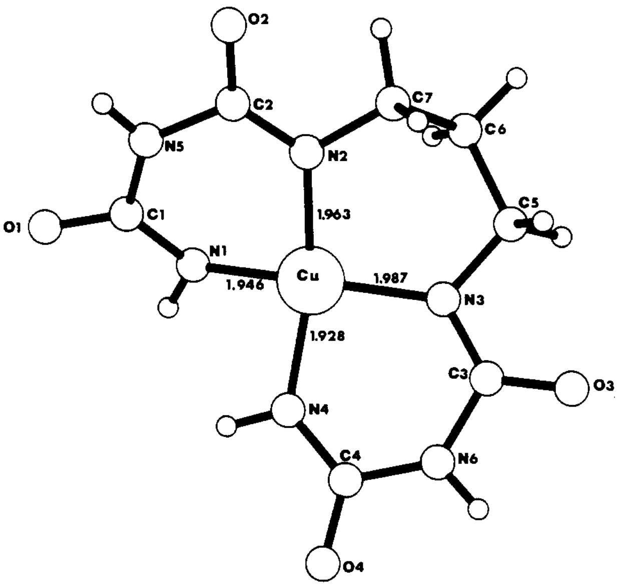

**Figure 5.** Drawing of the complex anion $[Cu(pr(bi)_2)]^{2-}$.

**Table VI.** Principal Bond Distances (Å) and Bond Angles (deg) for $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$

| | | | |
|---|---|---|---|
| (a) Coordination in Complex Anion | | | |
| Cu–N1 | 1.946 (4) | Cu–N3 | 1.987 (4) |
| Cu–N2 | 1.963 (4) | Cu–N4 | 1.928 (4) |
| N1–C1 | 1.321 (6) | C2–O2 | 1.258 (6) |
| C1–O1 | 1.257 (5) | C2–N2 | 1.311 (6) |
| C1–N5 | 1.388 (6) | N2–C7 | 1.460 (6) |
| N5–C2 | 1.411 (6) | | |
| C7–C6 | 1.494 (8) | C6–C5 | 1.523 (8) |
| C5–N3 | 1.466 (6) | N6–C4 | 1.376 (6) |
| N3–C3 | 1.324 (6) | C4–O4 | 1.262 (5) |
| C3–O3 | 1.264 (6) | C4–N4 | 1.312 (6) |
| C3–N6 | 1.401 (6) | | |
| N1–Cu–N2 | 89.3 (2) | N4–Cu–N1 | 89.5 (2) |
| N2–Cu–N3 | 97.7 (2) | N1–Cu–N3 | 160.7 (2) |
| N3–Cu–N4 | 91.5 (2) | N2–Cu–N4 | 155.3 (2) |
| (b) Coordination around Sodium Cations | | | |
| Na1–O1$^{I}$ | 2.363 (4) | Na1–OS2$^{III}$ | 2.422 (4) |
| Na1–O3$^{II}$ | 2.419 (4) | Na1–OS3$^{IV}$ | 2.570 (4) |
| Na1–O4 | 2.339 (4) | Na1–OS3$^{V}$ | 2.510 (4) |
| Na2–O1$^{VI}$ | 2.397 (4) | Na2–OS1$^{VI}$ | 2.303 (5) |
| Na2–O2 | 2.464 (4) | Na2–OS2 | 2.404 (4) |
| Na2–O3$^{VII}$ | 2.451 (4) | | |

**Table VII.** Comparison of the Biuret Parts: Mean Bond Distances (Å) and Bond Angles (deg)

| | $[Cu^{II}(pr(bi)_2)]^{2-}$ | $[Cu^{II}(ophen(bi)_2)]^{2-}$ | $[Cu^{III}(ophen(bi)_2)]^{-a}$ |
|---|---|---|---|
| Cu–N(term) | 1.937 (9)[b] | 1.917 (8) | 1.835 (15) |
| Cu–N(bridg) | 1.975 (12) | 1.962 (3) | 1.875 (15) |
| C–N(Cu)[c] | 1.317 (6) | 1.334 (14)[d] | 1.365 (10) |
| C–N | 1.394 (15) | 1.388 (8) | 1.355 (6) |
| N–C(bridg) | 1.463 (3) | 1.415 (6) | 1.410 (10) |
| C–O | 1.260 (3) | 1.252 (6) | 1.250 (14) |
| O–C–N(Cu) | 125.6 (9) | 126.5 (4) | 122.2 (15) |
| N–C–N(Cu) | 118.8 (7) | 118.3 (5) | 119.2 (19) |
| N–C–O | 115.5 (12) | 115.1 (4) | 118.5 (19) |

[a] See ref 5. [b] The standard deviation for the mean value is defined as $[\sum(\bar{x} - x)^2/(n - 1)]^{1/2}$. [c] N(Cu) means N atom bonded to Cu; N means not bonded to Cu. [d] See ref 16.

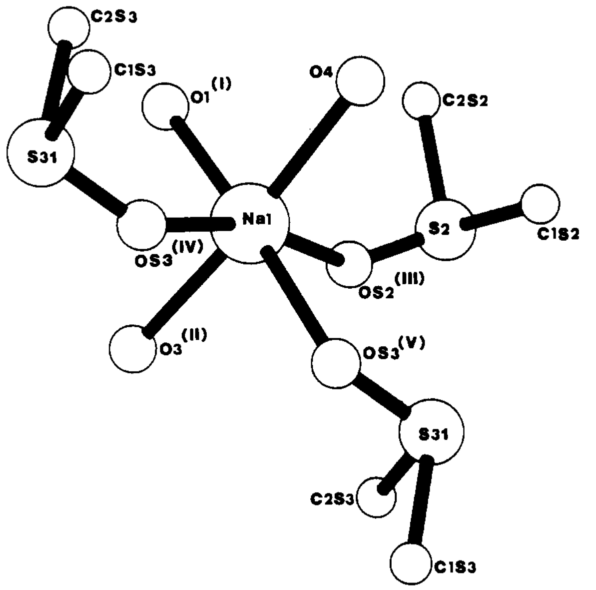

**Figure 6.** Coordination around sodium cation Na1 in $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$.

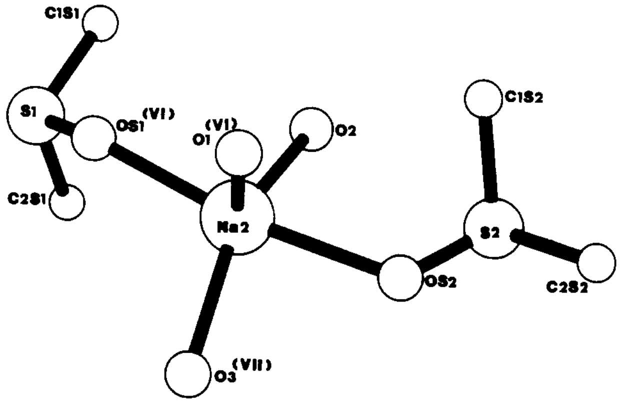

**Figure 7.** Coordination around sodium cation Na2 in $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$.

and in better agreement with other known Cu–N(peptide) distances.[14] This difference in Cu–N bond lengths reveals clearly the constraint due to the bridge between the two biuret parts. Another common feature is the difference between the two types of C–N bonds of the biuret part: the bond lengths with the noncoordinated N atoms are significantly larger, showing an electronic delocalization with the carbonyl groups weaker than the C–N(Cu) bonds.

An interesting comparison can be made with the $[Cu^{III}(ophen(bi)_2)]^-$ compound involving one of our ligands and published by Birker[5] (Table VII). The effects of the oxidation states of the copper atom on the structure of the complex are the following: (i) the same planar coordination for both complexes around the copper atom, the copper(III) compounds being slightly more tetrahedrally distorted;[15] (ii) shortening of the Cu–N bond lengths (0.09 Å) in the Cu(III) complex with subsequent modifications of the N–Cu–N angles, the N1–Cu–N4 angle being closed (91.7° in the Cu(II) complex compared to 86.4° in the Cu(III) complex) and the others being opened; (iii) modifications of the C–N bond lengths—lengthening of the C–N(Cu) bonds and shortening of the C–N(H) bonds in the Cu(III) complex; (iv) modifications of the angles around the carbon atoms, becoming closer to the $sp^2$ value of 120° in the Cu(III) complex. All these data indicate an electronic movement over the whole biuret parts of the ligand when the copper atom is oxidized.

Another recent example for comparison is given by a copper(III) tripeptide complex[17] which presents a $CuN_3O$ square-planar coordination with very short Cu–N(peptide) bond lengths (1.80 Å). The C–N(Cu) bonds are slightly lengthened as compared with those of Cu(II) compounds (1.34 vs. 1.31 Å) Margerum et al.[17] explain these structural changes (C–N bonds) by a delocalization of the carbonyl double bond in two resonance forms. In our case the C–O bonds are not affected by the oxidation state of the copper atom; thus it seems difficult to propose the same explanation.

**Electronic Spectra and Magnetic Data.** The electronic spectra and magnetic data of all compounds[18] are rather consistent with a square-planar geometry around the metallic ion. In the case of the low-spin cobalt(II) complex, several transitions are spin allowed between doublet states. Electronic spectra (Figure 9) show a narrow band near 1000 nm (1070 and 1000 nm for $[Co(ophen(bi)_2)]^{2-}$ and $[Co(en(bi)_2)]^{2-}$) and a strong and large band around 435 nm characteristic of a square-planar structure.[19] The other bands are d–d transitions with the exception of the most energetic band also present in the Cu(II) and Ni(II) compounds; this band is probably a charge-transfer band. In the cobalt(II) complex, the large orbital contribution to the magnetic moment (~2.3 $\mu_B$) can be explained by a distorted structure slightly away from the purely planar molecule or by the spin–orbit interaction between the lowest excited state $^2E_g$ and the $^2A_{1g}$ ground state.[20] X-ray powder diagrams show clearly that Cu, Ni, and Co complexes with the ophen(bi)$_2$ ligand are isomorphous, which is also an indication for a square-planar structure allowing nevertheless

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(14) For example 1.93 Å in potassium bis(biuretato)cuprate(II) from: Freeman, H. C.; Smith, J. E. W. L.; Taylor, J. C. *Acta Crystallogr.* **1961**, *14*, 407.

(15) The highest deviation from the mean plane $CuN_4$ for the copper(III) compound is 0.120 Å.

(16) A small delocalization effect with the phenyl group can be shown by slightly different bond lengths for terminal N atoms (1.321 Å) and for bridging N atoms (1.346 Å). The N–C(bridg) bonds are also shorter than the corresponding ones for the pr(bi)$_2$ ligand.

(17) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021.

(18) The exception of $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$ can be related with the higher magnetic moment of this complex.

(19) (a) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968. (b) Everett, G. W.; Holm, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 5261.

(20) Nishida, Y.; Kida, S. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 32.

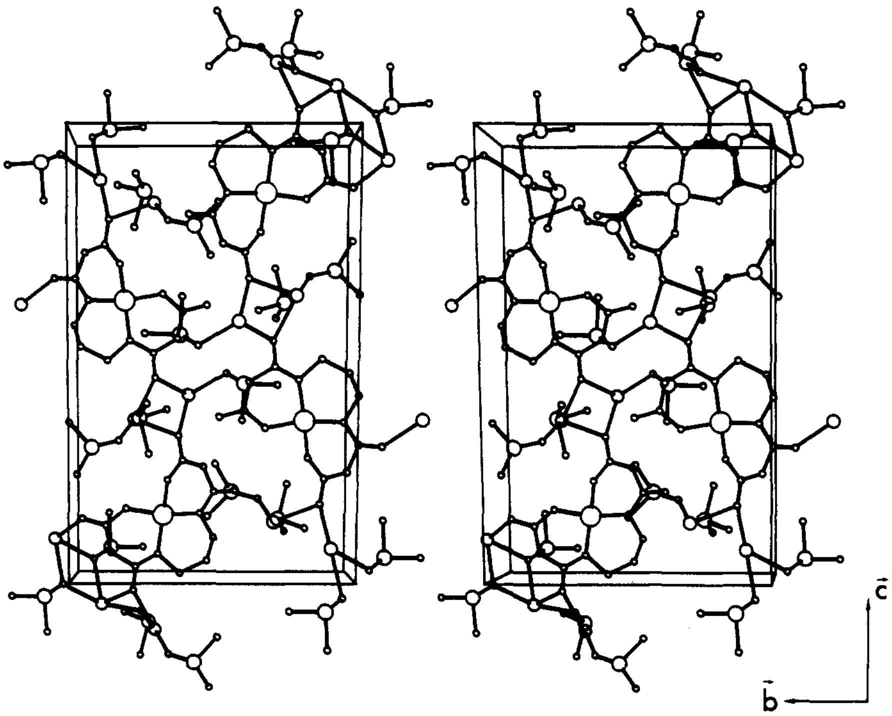

**Figure 8.** Stereoview of the packing for $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$.

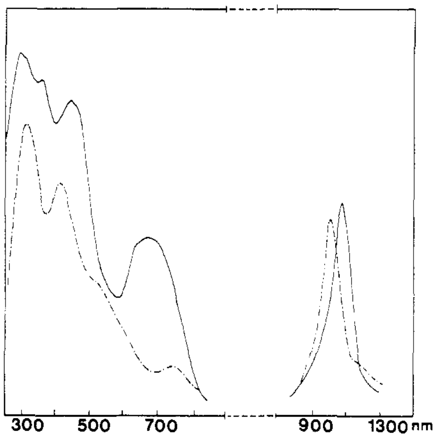

**Figure 9.** Electronic spectra: (solid line) $Na_2[Co(ophen(bi)_2)]$; (broken line) $Na_2[Co(en(bi)_2)]$.

the possibility of a slight distortion.

**Attempts of Oxidation.** Addition of iodine to a red $[Cu^{II}(ophen(bi)_2)]^{2-}$ or $[Cu^{II}(pr(bi)_2)]^{2-}$ solution (mixture of 80% $Me_2SO$, 20% $H_2O$) gives a green solution characteristic of Cu(III) compounds.[21] (Compounds with the $en(bi)_2$ ligand are insoluble in this solvent mixture.) The method of continuous variations is in agreement with the reaction

$$CuL^{2-} + {}^1/_2I_2 \rightarrow CuL^- + I^- \qquad L = ophen(bi)_2,\ pr(bi)_2$$

Electronic spectra of the stoichiometric solution ($10^{-2}$ M $Cu(ophen(bi)_2)$ and $5 \times 10^{-3}$ M $I_2$) and of the $[(n\text{-}C_4H_9)_4N][Cu^{III}(ophen(bi)_2)]\cdot CHCl_3$ solid compound described by Birker[5] are similar and confirm oxidation of Cu(II) to Cu(III) in solution. On the other hand, attempts to prepare the $Cu^{III}(pr(bi)_2)$ complex in the solid state were unsuccessful. These observations are in agreement with Margerum's hypothesis,[3] according to which oxidation of Cu(II) compounds is easier if the geometry around the metallic cation is not distorted from square planar.

In the case of Ni(II) compounds we can observe an oxidation of the complex with iodine (dark brown solutions), but the high oxidation states of the nickel atom are too unstable to permit a study. The solutions exhibit the previous orange-yellow color after a few minutes.

**Acknowledgment.** We wish to thank A. M. Hardy and Prof. A. Hardy (Laboratoire de Cristallochimie Minérale, Université de Poitiers) for diffractometer and computing facilities.

**Registry No.** $Na_2[Cu(ophen(bi)_2)]\cdot4Me_2SO$, 98014-83-6; $Na_2[Cu(en(bi)_2)]$, 98014-84-7; $Na_2[Cu(pr(bi)_2)]\cdot3Me_2SO$, 98049-96-8; $Na_2[Ni(ophen(bi)_2)]\cdot4Me_2SO$, 98014-86-9; $Na_2[Ni(en(bi)_2)]\cdot2Me_2SO$, 98014-88-1; $Na_2[Ni(pr(bi)_2)]\cdot3Me_2SO$, 98014-90-5; $Na_2[Co(ophen(bi)_2)]\cdot4Me_2SO$, 98049-98-0; $Na_2[Co(en(bi)_2)]$, 98014-91-6; $en(biH_2)_2$, 98014-92-7; $pr(biH_2)_2$, 98014-93-8; $ophen(biH_2)_2$, 98014-94-9.

**Supplementary Material Available:** Elemental analyses and $^1H$ NMR spectra of the ligands (Table SI), powder diffraction data (Table SII), anisotropic thermal vibration parameters (Tables SIII and SIV), interatomic distances and angles (Tables SV and SVI), and observed and calculated structure factors for the two structures (Tables SVII and SVIII) (39 pages). Ordering information is given on any current masthead page.

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(21) Barbier, J. P.; Hugel, R. P.; Kappenstein, C. *Inorg. Chim. Acta* **1983**, *77*, L117.