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Copper(III) and Nickel(III) Complexes of Biuret and Oxamide

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Bis-biuretato complexes of Cu(II) and Ni(II) KM(Rbi)₂ (where M is Cu or Ni, and Rbi is the dianion HNCONRCONHR) can be formed by deprotonation of the corresponding biuret, R = H or alkyl) can be oxidized to KM(Rbi)₂ in which the metal has the oxidation number III. Nmr, ir, and magnetic susceptibility studies of these compounds revealed that these ligands are bonded via their N atoms, most probably in a planar coordination around the metal. The oxidation occurs in aqueous solutions at a potential of 0.50-0.65 V (relative to a saturated calomel electrode); in DMSO the reaction is a reversible one-electron transfer at E₁/₂ = -0.35 V as shown by polarographic measurements. Two H₂O or Rbh molecules can be bonded to the coordinated biuretate groups, most probably via H bridges. A bis-oxamidato complex KCu(HNCOCONHR)₂ could be prepared with analogous properties. The stabilizing influence of these ligands on the high oxidation states of the metals is thought to be due to the very strong electron-donating capacity of the deprotonated amine groups.

Introduction

In a previous short communication we have reported the preparation and the properties of bis-biuretato complexes of Cu(III) and Ni(III) with compositions of KCu(bi)₂ and KNi(bi)₂, respectively, wherein bi is the dianionic ion HNCONHRCONHR formed by deprotonation of biuret (H₂NCONHRCONHR = biH₂). The further study of these compounds was seriously hampered by their extremely low solubility. We now succeeded in preparing analogous complexes derived from the alkyl-substituted biuret ions (of the type HNCONHRCONHR) which are soluble in acetone, alcohol, and DMSO, allowing a more detailed study. With respect to the oxidation to a Cu(III) complex the dianionic form of oxamide (HNCOCONHR = oxam) behaves in the same way as the biuretate ion. We shall report here about the preparation and the properties of these compounds in which Cu and Ni have the uncommon oxidation state III. The specific influence of the ligands leading to a stabilization of these high oxidation states will be discussed.

Experimental Part

K₂Cu(bi)₂, K₂Ni(bi)₂, and K₂Cu(oxam)₂ were prepared according to known methods.¹,²

Preparation of K₂Cu(bi)₂.—(a) A solution of K₂Cu(bi)₂ was prepared by dissolving 2.2 g of biuret, 2.5 g of CuSO₄·5H₂O, and 8 g of KOH in 25 ml of water. When an excess of K₂SO₄ was added to this solution, the compound KCu(bi)₂ precipitated immediately. The compound was filtered off, washed with hot water (70°), and dried in a vacuum desiccator.

(b) When the above-mentioned K₂Cu(bi)₂ solution was electrolyzed between Pt electrodes, KCu(bi)₂ was precipitated on the anode. The anode potential, measured with an auxiliary saturated calomel electrode, was 0.50 V. The compound was collected, washed with water, and dried.

(c) KCu(bi)₂ was formed when air with some hydrogen chloride was bubbled through a suspension of K₂Cu(bi)₂ in benzene. On further study, uv irradiation, formerly reported to be necessary,³ appeared to be redundant.

Anal. Calcd for KCu(bi)₂: Cu, 20.85; K, 12.84; C, 15.76; H, 1.97; N, 27.58. Found: Cu, 20.95; K, 12.72; C, 15.61; H, 2.02; N, 27.25 (for a sample prepared according to method a, the other methods give analogous results).

Preparation of K₂Cu(oxam)₂.—The procedures a and b, as described for KCu(bi)₂, but now starting with NiSO₄, were possible. Method b gave a very poor yield. The electrode potential, measured relative to saturated calomel electrode was 0.50 V. Preparation according to procedure c was impossible. Anal. Calcd for K₂Ni(oxam)₂: Ni, 19.57; K, 13.04; C, 16.02; H, 2.02; N, 28.01. Found: Ni, 19.60; K, 13.10; C, 16.22; H, 2.13; N, 27.25.

Preparation of K₂Cu(3-Rbi)₂·2H₂O.—The preparation of pure 3-alkylbiuret appeared to be very difficult. The recipe of Weith for the preparation of 3-phenylbiuret, modified to produce 3-alkylbiuret, yielded a mixture of products, among which were 3- and 1-alkylbiuret. The separation of 3-alkylbiuret was very difficult and will be published elsewhere. In the next sections we give methods to prepare K₂Cu(3-Rbi)₂·2H₂O, R = propyl, starting with pure propylbiuret and with the just mentioned reaction mixture.

(a) When 1 g of KOH was added to a solution of 0.5 g of CuSO₄·5H₂O and 1 g of propylbiuret in 10 ml of water, Cu-

4. W. Weith, Ber., 18, 1444 (1877).
(3-Rbi)²⁻ was formed. By electrolytic oxidation of this solution, KCu(3-Rbi)²⁻·2H₂O precipitated on the platinum anode (anode potential 0.65 V relative to the saturated calomel electrode). The product was rinsed with water, dried, and dissolved in acetone. After evaporation of the acetone, the complex was crystallized from an alcohol or DMSO solution by adding chloroform and ether.

(b) With this same procedure but using the above-mentioned reaction mixture of 1- and 3-propylbiuret (instead of pure 3-propylbiuret), the interesting product KCu(3-Rbi)(1-RbiH₂)₂ was obtained. If a DMSO solution of this complex was exposed to moist air for 24 hr, KCu(3-Rbi)²⁻·2H₂O could be precipitated by adding chloroform and ether. The preparation by oxidation of KCu(3-Rbi)²⁻ with K₃S₅O₃ or with air was not possible.

Preparation of KNi(3-Rbi)(1-RbiH₂).—The same procedure for the corresponding Cu complex could be used. The electrode potential was 0.65 V (relative to sce). Because the yield was very poor, the product could only be identified by its ir spectrum being identical with that of the analogous Cu complex.

Preparation of KCu(oxam)⁺.—By electrolytic oxidation of a slurry of 3 g of oxamide in a solution of 1 g of K₂CO₃ in 50 ml of 0.1 N KOH (electrode potential of 0.55 V (relative to sce), KCu(oxam)⁺ precipitated as a yellow product on the anode. The product could be purified from coprecipitated copper oxide by rinsing it fast with 1 N HCl, which dissolved the copper oxide much faster than the KCu(oxam)⁺. The complex was decomposed when exposed to light. Anal. Calcd for KCu(3-Rbi)(1-RbiH₂): Cu, 23.12; C, 35.36; H, 5.22. Found: Cu, 23.01; C, 34.50; H, 6.40. Anal. Calcd for KCu(3-Rbi)(1-RbiH₂): Cu, 23.12; C, 35.36; H, 5.22. Found: Cu, 23.01; C, 34.50; H, 6.40.

Results and Discussion

The oxidation of the biuretato complexes of Cu(II) and Ni(II) to the respective Cu(III) and Ni(III) compounds and of the Cu(II) oxamidato to the copper(II)–oxamidato complex is possible in alkaline solutions at oxidation potentials of 0.7–0.9 V. This is in agreement with the results of Levitzki and Anbar, who estimated the oxidation potential of the reaction Cu(bi)²⁻ → Cu(bi)³⁻ + e⁻ to be between 0.85 and 1.07 V. These high potentials are about the limit


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of what is possible in aqueous alkaline solutions. Slight modifications in the ligands cause the synthesis to fail; despite considerable effort, we did not succeed in preparing the oxamidato complex of Ni(III) and 3-phenylbiuretato and malondiamidato complexes of Cu(III) and Ni(III). We think that the specific influence of the biuretato and oxamidato ligands is primarily due to the strong electron-donating power of the deprotonated amine groups in these ligands. These cause a very high electron density on the metal ion, facilitating its oxidation. The Cu compounds are more easily oxidized than those of Ni. The base strength of the ligands required for a stable oxidation product must be between an upper and a lower limit. When the base strength of the anion is very high, no deprotonation of the amine can occur; below a certain base strength the oxidation is impossible. Obviously the limits are also dependent on the redox as well as on the acidic properties of the solvent. Due to solubility problems however no other solvent than water could be investigated. Most amines, aliphatic or aromatic, are too weak acids to deprotonate, even in strongly alkaline solutions. The neighboring C=O groups in biuret and oxamide apparently give a situation just between the critical limits. The failure to prepare the 3-phenylbiuretato complexes of Cu(III) and Ni(III) must then be ascribed to the electron-withdrawing capacity of the phenyl groups, which decrease the base strength of the ligand below the critical value for which oxidation of the metal is possible. Although deprotonation and complexation of malondiamide to Cu(II) was demonstrated by Rising, Hicks, and Moerke, the impossibility to oxidize that complex is probably due to the lack of $\pi$ delocalization, which certainly also contributes to the stability of the biuretato and oxamidato compounds.

Nmr spectra of the copper-biuretato complexes show them to be coordinated via the N atoms (see Table III). This same can be concluded from the ir spectra of all Cu(III) and Ni(III) complexes, using the criterion given by McLellan and Kedzia. The oxamidato complexes of Cu(II) and Ni(II) are coordinated via N atoms as was established by the interpretation of ir spectra. Since the ir spectrum of KCu(oxam)$_2$ resembles closely that of K$_2$Cu(oxam)$_2$, we think their structures to be similar (see Figure 1). X-Ray crystal work has shown that the bis-biuretato complex of Cu(II) is planar. For the bis(biuretato)-nickel(II) complex planarity was concluded on the basis of the diamagnetism and ir and electron spectroscopic data. A detailed study of the ir spectra of the oxamidato complexes of Cu(II) and Ni(II) points out a planar structure for these compounds. We think the newly prepared Cu(III) and Ni(III) complexes also to be planar, a conclusion mainly based on the observed magnetic data, the Cu(III) complexes being diamagnetic and the Ni(III) complexes paramagnetic according to one unpaired electron spin.

The polarographic half-wave potentials of the oxida-
tion and reduction waves of the Cu(III) and Cu(II) compounds, respectively, are practically identical. This fact, as well as the observed linearity of the log \( [i/ (i_d - i)] \) vs. \( E \) plot, reveals that both compounds can be interconverted by a reversible one-electron step \( (i_d = \text{diffusion current}) \). This reversibility strongly suggests that both complexes have very similar structures, \( \text{viz.} \), planar four-coordination as illustrated in Figure 2.

The data of the electronic spectra of KCu(bi)\(_2\) and KCu(oxam)\(_2\), together with those of the isoelectronic Ni(II) species, are given in Table V. This similarity in these spectra give support to the idea of the structural similarity of these compounds. Regarding the structure of the Ni(III) complexes, however, no more evidence is available at the moment.

From a structural point of view these compounds are thus much like the series of MN\(_4\) complexes reported by Balch and Holm.\(^9\) The ligand in these series (where \( n \) can vary from 2\( - \) to 2\( + \)) is \( \text{o-} \cdot \text{C}_\text{6} \text{H}_\text{4} (\text{NH})_\text{2} \), which can exist in two forms of different oxidation state, \( \text{viz.} \), as the dianion of \( \text{o-phenylenediamine} \) and as \( \text{o-benzoquinonediimine} \). This fact is strongly related to the characteristic properties of these series of metal complexes. Since different oxidation forms of the dianions of biuret and oxamide are obviously not possible, we think them to be representatives of a different class of ligands.

The structure of the interesting compounds KM-(3-Rbi)\(_2\)(1-RbiH\(_2\))\(_2\) is not definitely established. Nmr data (see Table IV) and ir spectra show that the 1-propyliuret is not deprotonated and not coordinated to the metal. The identical uv spectra and magnetic properties of KCu(3-Rbi)\(_2\)·2H\(_2\)O and KCu(3-Rbi)\(_2\)·(1-RbiH\(_2\))\(_2\) indicate also that there is no coordination of 1-Rbi or H\(_2\)O to the Cu. Extensive H bridging is a characteristic feature of the chemistry of the biurets so we think that the two 1-propyliuret molecules are H bonded to the biuretato ligands, probably \( \text{via} \) the 3-NH groups, because when these places are blocked by substituting an alkyl group, no extra biurets are found to be bonded to the complexes. The two H\(_2\)O molecules in KCu(3-Rbi)\(_2\)·2H\(_2\)O are probably bonded in the same way.

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