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Spin-Triplet Cobalt Complexes of Biuret and Related Ligands

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A number of planar Co\textsc{iii}N\textsc{v} complexes have been prepared with biuret and N-substituted biurets. They are shown to have triplet electronic ground states in the temperature range 6.4–293°K. The zero-field splitting is estimated to be about 40 cm\textsuperscript{-1}. The triplet ground state is consistent with molecular orbital energies obtained from extended Hückel calculations. The d\textsubscript{xy} and d\textsubscript{yz} orbitals both have the same energy and are both occupied by one electron. Polarographic measurements show that these complexes can be reversibly reduced in a one-electron step. With amines, diamagnetic six-coordinated mixed-ligand species are obtained, whose uv-vis spectra can be interpreted as for Co(III) in an octahedral environment.

Introduction

In previous communications from our laboratory the rather unique properties of biuret as a ligand were discussed. It was shown that the well-known Cu(II) and Ni(II) complexes could be oxidized with various oxidizing agents yielding the corresponding Cu(III) and Ni(III) compounds.\textsuperscript{1,2} With cobalt the very remarkable planar bis(biuretato)cobalt-

Experimental Part

**Abbreviations.** Abbreviations used in this paper are as follows: bi = [HNCONHCONH]²⁻, 3-Pr(bi) = [HNCON(C₃H₇)CONH]²⁻, 3-Pr(bi)₃ = [HNCON(C₃H₇)CONH]³⁻, 1-Pr(bi)H₂ = H₂NCONHCONH₂

**Syntheses.** o-Phenylenbis(biuret) and Ethylenebis(biuret).

These ligands were obtained in a way analogous to the method used for the preparation of 1-alkyl-substituted biuret⁴ starting with a 2:1 mixture of nitrobiuret and o-phenylenediamine or ethylenediamine, respectively.

KCo(bi). Cobalt acetate (25 g) was dissolved in 25 ml of water. Biuret (30 g) and KOH (36 g, dissolved in 50 ml of water) were added to this solution and the resulting blue slurry was oxidized with air during 24 hr. The insoluble material was then removed by filtration and upon careful neutralization with 6 N HCl to pH 7 KCo(bi)₂ precipitated as a yellow compound. It was filtered off, washed with water, and dried in a vacuum desiccator. The compound is insoluble in any solvent.

**Anal.** Calc'd for KCo(bi)₂: K, 13.03; Co, 19.65; C, 16.00; H, 2.00; N, 28.00. Found: K, 13.4; Co, 19.5; C, 15.7; H, 2.2; N, 27.2.

KCo(3-Pr(bi))₂. 3-Phenylbiuret was prepared according to Weith⁶ for the preparation of 3-phenylbiuret is used for the preparation of alkylbiurets, a mixture of 1-alkylbiuret and 3-alkylbiuret is always obtained. So when a mixture of 0.1 mol of very dry propyleneurea and 0.1 mol of PCl₃ is refluxed during 4 hr, a acid solution containing 1-alkylbiuret and 3-alkylbiuret is obtained after hydrolysis of the reaction mixture with ice. In such a solution excess CoCl₂· 6H₂O was dissolved. KOH was added until a blue slurry was formed, which was oxidized with air during 24 hr. The precipitate was filtered off and upon careful neutralization with the red solution, with 6 N HCl to pH 7, the yellow complex precipitated. It was filtered off and washed with water. The complex is soluble in DMSO, alcohol, and acetone.

**Anal.** Calc'd for KCo(3-Pr(bi))₂(1-Pr(bi)H₂)₂: Co, 8.73; C, 35.51; H, 5.98; N, 24.92. Found: Co, 8.5; C, 35.2; H, 6.1; N, 25.0.

In an analogous way other compounds of composition KCo(3-alky(bi))₂(1-alky(bi)H₂)₂ could be prepared.

KCo(3-Pr(bi))₂· 2H₂O. From a solution of KCo(3-Pr(bi))₂(1-Pr(bi)H₂)₂ in moist DMSO the compound KCo(3-Pr(bi))₂· 2H₂O precipitated upon addition of chloroform and ether. It was filtered off and washed with chloroform.

**Anal.** Calc'd for KCo(3-Pr(bi))₂· 2H₂O: Co, 14.0; C, 28.6; H, 5.3; N, 19.9. Found: Co, 13.9; C, 28.6; H, 4.9; N, 18.8.

KCo(3-Pr(bi))₂· 2DMSO. In dry DMSO KCo(3-Pr(bi))₂(1-Pr(bi)H₂)₂ was dissolved. After a few hours KCo(3-Pr(bi))₂· 2DMSO could be precipitated by adding dry chloroform. The precipitate was filtered off and washed with chloroform in dry air as it is sensitive to moisture.

**Anal.** Calc'd for KCo(3-Pr(bi))₂· 2DMSO: C, 31.11; H, 5.59. Found: C, 30.9; H, 5.9.

KCo(en(bi)₂). Ethylenebis(biuret) (1.2 g) and cobalt acetate (1.2 g) were dissolved in 40 ml of DMSO. To this solution 1.2 g of KOH dissolved in 4 ml of water was added. This mixture was oxidized with air during 3 hr. The precipitate was filtered off and washed with alcohol. It was dissolved in a lot of warm DMSO. The insoluble material was removed by filtration, and after cooling, the compound could be precipitated by adding a large amount of chloroform. The precipitate was filtered off and washed with chloroform.

**Anal.** Calc'd for KCo(en(bi)₂): C, 22.01; H, 2.46; N, 25.7. Found: C, 22.0; H, 2.7; N, 25.0.

KCo(o-phen(bi)₂). Ethylenebis(biuret) (0.75 g) and o-phenylenebis(biuret) (0.85 g) were dissolved in 60 ml of DMSO. KOH (1 g dissolved in 6 ml of water) was added. This mixture was oxidized with air during 2 hr. The solution was filtered and the purple complex was precipitated from the filtrate by adding alcohol. The compound was filtered off and dissolved in DMSO. The solution was filtered, and the complex was again precipitated with alcohol and ether, filtered off, and washed with alcohol.

**Anal.** Calc'd for KCo(o-phen(bi)₂): C, 32.09; H, 2.15; N, 22.46. Found: C, 31.6; H, 2.3; N, 22.1.

Bu₄NCo(en(bi)₂). Cobalt acetate (1.2 g) was dissolved in a mixture of 20 ml of water and 10 ml of DMSO. Ethylenebis(biuret) (1.2 g) and 12.5 ml of a 40% Bu₄NOH solution in water were added and the resulting blue slurry was oxidized with air during 12 hr.
Table I. Spectral and Magnetic Data of Triplet Cobalt Complexes

<table>
<thead>
<tr>
<th>Compd</th>
<th>Meas temp range over which Curie-Weiss law is obeyed, °C</th>
<th>( \Theta, ^\circ C )</th>
<th>( \nu_3, \text{kHz} )</th>
<th>( \nu_4, \text{kHz} )</th>
<th>( \nu_5, \text{kHz} )</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCo(bi)</td>
<td>-150 to +100</td>
<td>0</td>
<td>13.3 sh</td>
<td>12.6 (100)</td>
<td>11.6 (50)</td>
<td>Solid KBr</td>
</tr>
<tr>
<td>Bu₄NCo(bi)₂</td>
<td>-150 to +100</td>
<td>-4</td>
<td>13.3 sh</td>
<td>12.2 (107)</td>
<td>11.5 (51)</td>
<td>DMSO</td>
</tr>
<tr>
<td>KCo(3-Pr(bi))₂(1-Pr(bi)H₂)</td>
<td>-150 to +100</td>
<td>0</td>
<td>13.4 sh</td>
<td>12.8 (107)</td>
<td>11.5 (51)</td>
<td>Solid KBr</td>
</tr>
<tr>
<td>KCo(3-Pr(bi))₂-CHCl₃</td>
<td>-150 to +100</td>
<td>0</td>
<td>13.7 sh</td>
<td>12.6 (100)</td>
<td>11.6 (50)</td>
<td>DMSO</td>
</tr>
<tr>
<td>KCo(3-Pr(bi))₂-2DMSO</td>
<td>-150 to +100</td>
<td>-16</td>
<td>13.0 (140)</td>
<td>12.2 sh</td>
<td>11.5 (40)</td>
<td>DMSO</td>
</tr>
<tr>
<td>Bu₄NCo(bi)₂</td>
<td>-150 to +100</td>
<td>-19</td>
<td>13.8 (1240)</td>
<td>12.2 (600)</td>
<td>11.2 (600)</td>
<td>DMSO</td>
</tr>
<tr>
<td>Bu₄NCo(o-phen(bi)₂)</td>
<td>-150 to +100</td>
<td>-19</td>
<td>13.8 (1200)</td>
<td>12.2 (600)</td>
<td>11.2 (600)</td>
<td>DMSO</td>
</tr>
<tr>
<td>Bu₄NCo(o-phen(bi)₂)-CHCl₃</td>
<td>-150 to +100</td>
<td>-19</td>
<td>13.8 (1200)</td>
<td>12.2 (600)</td>
<td>11.2 (600)</td>
<td>DMSO</td>
</tr>
</tbody>
</table>


The precipitate of the crude red complex was then filtered off. It was dissolved in DMSO, the solution was filtered, and small purple needles of the pure complex were observed. The solution was then oxidized with air during 0.5 hr. The purple precipitate of the crude complex was filtered off. It was dissolved in DMSO, the solution was filtered, and small purple needles of the pure complex were obtained.

All these complexes do not have good melting points but decompose in general above 170°.

Physical Measurements. Magnetic susceptibilities were measured with a Gouy type equipment with HgCo(NCS)₄ as a reference over a temperature range of -150 to +20°. A vibrating-sample magnetometer (Princeton Applied Research Type 155) equipped with a ter (Princeton Applied Research Type 155) equipped with a dropping mercury electrode was used as solvent with 0.1 N, amines) unfavorable, while there is in the case of the biuretato complexes no indication of coordination with weak electron donors (e.g., H₂O, DMSO, alcohol). Sometimes, however, the solid compounds contain DMSO, H₂O, or 1-alkylbiuret. It has been shown by crystallographic structure determination that the 1-alkylbiuret molecules are not coordinated with the cobalt atom and that the cobalt atom is in planar coordination with four nitrogen atoms of deprotonated 3-alkylbiurets. Through formation of H bridges the 1-alkylbiuret molecules are incorporated in the crystal lattice around the potassium ions, yielding compounds which can at best be formulated as [K(1-alkyl(bi)H₂)₂][Co(3-alkyl(bi))₂]. Compounds of this composition are insoluble in water, so the coincidental presence of 1-alkylbiuret in the reaction mixture from which these compounds are prepared (see Experimental Part) enabled us to prepare these compounds from aqueous solutions. The CoN₄ complexes that are soluble in water (e.g., KCo(3-Pr(bi))₂-2DMSO) are decomposed in neutral or acid solution, due to protonation of the ligand, so they have to be prepared in nonaqueous solvents such as DMSO. We believe that the cobalt atom in the solid compounds containing DMSO or H₂O is also four-coordinated, as the spectral and magnetic properties of these compounds are similar to those of the compound containing 1-alkylbiuret (see Table I and Figure 1).

Figure 1. Electronic spectrum of KCo(3-Pr(bi))₂(1-Pr(bi)H₂)₂ in DMSO.
Spin-Triplet Cobalt Complexes of Biuret

Table II. UV Spectral Data of Some Mixed-Ligand Complexes

<table>
<thead>
<tr>
<th>Compd</th>
<th>$\nu_1$, kK</th>
<th>$\nu_2$, kK</th>
<th>10$D_q$, kK</th>
<th>$B$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(3-Pr(bi))$_2$(NH$_3$)$_2$</td>
<td>20.4 (70)</td>
<td>27.4 sh</td>
<td>21.4</td>
<td>500</td>
</tr>
<tr>
<td>Co(3-Pr(bi))$_2$(C$_3$H$_7$NH$_2$)$_2$</td>
<td>18.5 (45)</td>
<td>27.8 sh</td>
<td>19.0</td>
<td>730</td>
</tr>
<tr>
<td>Co(3-Pr(bi))$_2$(pyrrolidine)$_2$</td>
<td>17.4 (42)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(3-Pr(bi))$_2$(py)$_2$</td>
<td>18.2 (47)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When excess of an amine is added to an alcoholic solution of these paramagnetic cobalt complexes, diamagnetic six-coordinated adducts are formed.$^3$ They can be isolated by adding ether to such a solution. These adducts are thermally unstable in the solid phase. They lose two amine molecules as was indicated by a gravimetric determination at 80°C and the parent four-coordinated paramagnetic complex is left.

The uv-vis spectra of these CoN$_4$L$_2$ compounds can readily be interpreted as for Co(III) in an octahedral environment (see Table II and Figure 2).

The magnetic moments of all the planar CoN$_4$ compounds indicate a triplet ground state. Their magnetic susceptibilities obey the Curie-Weiss law over a temperature range of -150 to +20°C. The susceptibility of KCo(3-Pr(bi))$_2$·2H$_2$O has been measured from 6.45 to 300°C. Below 40°C the magnetic susceptibility clearly deviates from the Curie-Weiss behavior (see Figure 3).

With the usual spin Hamiltonian for describing spin-triplet states the energy levels of a spin triplet in a magnetic field are obtained as given by Ballhausen.$^8$

Writing square root terms of the type

$$\frac{1}{2\sqrt{(D + E)^2 + \frac{4}{3}g_x^2B^2H_x^2}} = \frac{1}{2[D + E/2] + \frac{1}{3}g_x^2B^2H_x^2}$$

all symbols having their usual significance, the energies of these levels can be written as a constant plus a function of $H^2$, so in the general form

$$U_n = U_n(0) + U_n(1)H + U_n(2)H^2$$

$U_n(1)$ is always zero in these cases. Now inserting these values into van Vleck's formula

$$\chi_M = \frac{\sum_n (-U_n(0)/kT) \exp(-U_n(0)/kT)}{N\Sigma_n}$$

it is possible to write down expressions for $\chi_{Mx}$, $\chi_{My}$, and $\chi_{Mz}$ (i.e., $\chi_M$ when all the molecules have their $x$, $y$, or $z$ axis, respectively, parallel with the magnetic field). The bulk susceptibility of the powdered sample will then be

$$\chi_M = \frac{\chi_{Mx} + \chi_{My} + \chi_{Mz}}{3}$$

This results in

$$\chi_M = \frac{NB^2}{3} \left[ 1 + \exp\left(-\frac{D + E}{kT}\right) + \exp\left(-\frac{D - E}{kT}\right) \right]$$

At low temperatures this expression for $\chi_M$ approximates

$$\chi_M = \frac{2NB^2}{3} \left( \frac{g_x^2}{D + E} + \frac{g_y^2}{D - E} \right)$$

This means that at low temperatures $\chi$ is independent of the temperature which is in agreement with our measurements. In order to obtain a rough estimate for the value of $D$, we set $E$ equal to zero and take for $g_x$ and $g_y$ the value of 2. The measured constant low-temperature $1/\chi_M$ equals 29.3 so $D = 81.4 \times 10^{-16}$ erg = 40.9 cm$^{-1}$.

This zero-field splitting value is of the same order of magnitude as found by Dale$^{10}$ for iron(II) phthalocyanine where $D = 69.9$ cm$^{-1}$. At higher temperatures the expression for $\chi_M$ approximates

$$\chi_M = \frac{2NB^2}{3} \left( \frac{g_x^2}{D + E} + \frac{g_y^2}{D - E} \right)$$

This formula has the Curie-Weiss form $\chi = C(T - \Theta)$ which is also in agreement with our measurements.

Extended Huckel molecular orbital calculations are consistent with a triplet ground state for these planar CoN$_4$ complexes. The calculations were carried out using the VSIP's published by Basch, et al.,$^{11}$ as diagonal elements $H_{ii} = (ao_i)^2/(\lambda a0_i)$ in the Hamiltonian matrix and using the Wolfsberg-Helmholz approximation for the estimation of

Atomic orbitals were described by single-ξ Slater-type orbitals for $s$ and $p$ orbitals with $ξ$ values taken from Clementi and Raimondi and from Richardson, et al., and double-ξ functions were used for the description of the Co 3d orbitals taken from Richardson, et al. The MO diagram of the unsubstituted Co(bi)$_2^+$ ion was calculated using interatomic distances as in the alkyl-substituted complex. Assuming $D_{2h}$ symmetry, average values were used for the bond lengths. The cartesian axes system used is given in Figure 4. Iterative calculations were performed using a charge criterion of 0.002. Three different values for the Wolsberg-Helmholz parameter $K$ were used (2.50, 2.00, 1.75). The $d$ orbitals show little overlap with ligand orbitals. There are five molecular orbitals which have very large coefficients for the Co 3d atomic orbitals and they can be considered as almost pure $d$ orbitals (see Table III). The energy difference between these molecular orbitals appeared to be strongly dependent on the value of $K$. Quantitative correlation between observed spectra and calculated $d$-orbital splittings cannot be expected to exist due to the inherent inaccuracy in the Huckel approximation. The most important result of these calculations is that the $d_{xz}$ and $d_{yz}$ orbitals have almost the same energy for all values of $K$ (see Table III). The configuration ($d^7$) of the MO that largely consists of Co 3d* atomic orbital and all ligand $pz$ orbitals, has no center of symmetry in contrast with the situation in any other of the compounds reported here. In the latter no extensive delocalization over the ethylene bridge is possible. In the o-phenylenebis(biuret) complex with that of the o-phenylenebis(biuret) complex.

As the molecular orbitals in which the unpaired electrons are present have $xz$ and $x^2 - y^2$ symmetry, the electronic ground state in $D_{2h}$ symmetry is $^3$B$_2g$. All compounds have $D_{2h}$ symmetry except the o-phenylenebis(biuret) complex. In the latter no extensive delocalization over the ethylene bridge is possible. In the o-phenylenebis(biuret) complex the $xz$ molecular orbital, consisting of the Co 3d$_{xz}$ atomic orbital and all ligand pz orbitals, has no center of symmetry in contrast with the situation in any other of the compounds reported here. So some transitions involving this orbital will no longer be Laporte forbidden. This accounts for the larger extinction coefficients found for some of the d-d transitions in the o-phenylenebis(biuret) complex.

Table III. Coefficients of Co 3d Atomic Orbitals in the Four Highest Filled and the First Empty Molecular Orbitals, together with the Energies of these Orbitals for Different Values of the Wolsberg-Helmholz Parameter $K$

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>0.93382</td>
<td>-4.01319</td>
<td>0.94451</td>
<td>-8.05548</td>
<td>-0.94919</td>
<td>-10.86347</td>
</tr>
<tr>
<td>2.00</td>
<td>0.95914</td>
<td>-9.13753</td>
<td>-0.93858</td>
<td>-11.68261</td>
<td>-0.90342</td>
<td>-13.76943</td>
</tr>
<tr>
<td>1.75</td>
<td>0.98489</td>
<td>-9.13893</td>
<td>0.98419</td>
<td>-11.68973</td>
<td>-0.98145</td>
<td>-13.76865</td>
</tr>
</tbody>
</table>

Table IV. Coefficients of pz Atomic Orbitals of Ligand Atoms in the MO that Largely Consists of Co 3d* Orbital

<table>
<thead>
<tr>
<th>Compd</th>
<th>$E_{1/2}$, V</th>
<th>$E_{1/2} - E_{1/4}$, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCo(3-Pr(bi))$_2$</td>
<td>-0.71</td>
<td>60</td>
</tr>
<tr>
<td>KCo(3-Ph(bi))$_2$</td>
<td>-0.64</td>
<td>58</td>
</tr>
<tr>
<td>Bu$_4$NCoo(bi)$_2$</td>
<td>-0.65</td>
<td>64</td>
</tr>
<tr>
<td>Bu$_4$NCo(en(bi))$_2$</td>
<td>-0.63</td>
<td>60</td>
</tr>
<tr>
<td>KCo-o-phen(bi)$_2$</td>
<td>-0.47</td>
<td>60</td>
</tr>
</tbody>
</table>

Table V. Polarographic Data

- All potentials were measured with 0.1 $N$ Bu$_4$NClO$_4$ as supporting electrolyte. All waves were of the reduction type.
- Theoretical value: $(2RT/F) \ln 9$. At 20°C this value is 55.5 mV for a reversible one-electron transfer.

transferred through the delocalized $\pi$-electron system up to the cobalt atom (see Table V). The influence of a $\pi$-electron-withdrawing substituent on the 1 position has a much more pronounced effect as can be seen in Table V comparing the half-wave potentials of the ethylenebis(biuret) complex with that of the o-phenylenebis(biuret) complex.

Conclusions

The paramagnetic ($S = 1$) cobalt(III)-bis(biuretato) complexes show a normal Curie-Weiss magnetic behavior from room temperature down to $-150^\circ$. Below 50 K deviation from the Curie-Weiss behavior occurs due to zero-field splitting but the triplet ground state is not affected. The unpaired electrons are largely localized in the Co 3d$_{xz}$ and 3d$_{yz}$ atomic orbitals. The polarographic half-wave po-
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tentials are dependent on the nature of substituents on the
biuret ligand probably due to electron donating or with-
drawing through the delocalized π-electron system which
overlaps with the Co 3d_{xz} orbital.

Registry No.  KCo(bi)_2, 38637-46-6; KCo(3-Ph(bi))_2·
2DMSO, 38637-47-7; Bu_4NCo(3-Ph(bi))_2, 38637-48-8;
Bu_4NCo(bi)_2·H_2O, 38637-49-9; KCo(3-Pr(bi))_2·(1-Pr(bi)H)_2, 36472-84-1; KCo(3-Pr(bi))_2·2H_2O, 38637-51-3; KCo(3-Pr-
(bi))_2·2DMSO, 38637-52-4; KCo(en(bi))_2, 38637-53-5; KCo-
(o-phen(bi))_2, 38637-54-6; Bu_4NCo(en(bi))_2, 38637-55-7;
Bu_4NCo(o-phen(bi))_2·CHCl_3, 38637-56-8; KCo(3-Pr(bi))_2·
(NH_3)_2, 31282-33-4; KCo(3-Pr(bi))_2(C_9H_7NH_2)_2, 31282-34-
5; KCo(3-Pr(bi))_2(pyrrolidine)_2, 31249-56-6; KCo(3-Pr(bi))_2-
(pyridine)_2, 31240-71-8.

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opportunity to perform magnetic measurements below
150°K. We thank Dr. P. van der Put for help with the inter-
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