Spin-Triplet Cobalt Complexes of Biuret and Related Ligands

P. J. M. W. L. Birker, J. J. Bour, and J. J. Steggerda

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A number of planar CoIII(N) 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⁻¹. The triplet ground state is consistent with molecular orbital energies obtained from extended Hückel calculations. The \( d_{xz} \) and \( d_{yz} \) 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.¹,² With cobalt the very remarkable planar bis(biuretato)cobalt-

ate(III) ion could be synthesized having a spin-triplet ground state.\(^1,3\) The crystal structure of the 3-alkyl-substituted biuret complex of Co(III) was recently published.\(^4\) We now report more details about the properties of a series of cobalt complexes with biuret and related ligands.

**Experimental Part**

**Abbreviations.** Abbreviations used in this paper are as follows:

- bi = [HINCONHCNH\(^2\)]; 3-Pr(bi) = [HINCONC\(_2\)H\(_3\)CNH\(^2\)]; 3-Pr(bi) = [HINCON(C\(_3\)H\(_7\))CNH\(^2\)]; 1-Pr(bi)H\(_2\) = H\(_2\)NCONHCONHC\(_3\)H\(_2\).

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

These ligands were obtained in a way analogous to the method used for the preparation of 1-alkyl-substituted biuret\(^5\) starting with a 2:1 mixture of nitrobiuret and o-phenylenediamine or ethylenediamine, respectively.

**KCo(bi)\(_2\).** Cobalt acetate (25 g) was dissolved in 25 ml of water. Biuret (30 g) and KOH (35 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.

**Bu\(_4\)NCo(bi)\(_2\)-H\(_2\)O.** Calculated for Bu\(_4\)NCo(bi)\(_2\)-H\(_2\)O: Co, 8.5; C, 35.2; H, 5.9; N, 24.92. Found: Co, 8.5; C, 35.2; H, 5.8; N, 25.0.

In an analogous way other compounds of composition KCo(3-alkyl(bi))(1-alkyl(bi)H\(_2\))\(_2\) could be prepared.

**KCo(3-Pr(bi))\(_2\)-2H\(_2\)O.** From a solution of KCo(3-Pr(bi))(1-Pr(bi)H\(_2\)) in moist DMSO the compound KCo(3-Pr(bi))(2H\(_2\)) precipitated upon addition of chloroform and ether. It was filtered off and washed with chloroform and ether, filtered off, and washed with chloroform.

**Bu\(_4\)NCo(en(bi)\(_2\)).** Cobalt acetate (1.2 g) was dissolved in 100 ml of water. Biuret (6 g) and 75 ml of a 40% Bu\(_4\)NOH solution in water were added. The resulting mixture was filtered and the red filtrate was concentrated as described above with alcohol and ether after yielding a red precipitate, that was dissolved in DMSO. Add an aqueous 1 N HCl to this solution until the color had turned to orange-yellow. The complex was then precipitated by adding a little alcohol and much ether.

The precipitate was filtered off. It was dissolved in chloroform, the solution was filtered, and the complex was again precipitated by adding ether.

**Anal.** Calculated for Bu\(_4\)NCo(3-Ph(bi))\(_2\): C, 58.61; H, 7.69; N, 14.05. Found: C, 58.2; H, 7.7; N, 14.5.

Bu\(_4\)NCo(bi)H\(_2\)-H\(_2\)O (5 g) was dissolved in 200 ml of water. Biuret (6 g) and 75 ml of a 40% Bu\(_4\)NOH solution in water were added. The resulting mixture was filtered with air during 4 hr. The insoluble material was filtered off and the red filtrate was concentrated with alcohol and ether as described above until a volume of about 20 ml of the red solution was left. To this solution 50 ml of DMSO was added and 1 N HCl was dropped into the solution until the color of the solution was orange-yellow. The complex was precipitated by adding alcohol and ether and filtered off.

For purification it was dissolved in DMSO, the solution was filtered, and the complex was again precipitated with chloroform and ether, filtered off, and washed with chloroform.

**Anal.** Calculated for Bu\(_4\)NCo(en(bi)\(_2\)): C, 46.0; H, 8.4; N, 18.8. Found: C, 45.6; H, 7.9; N, 18.8.

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 2 hr. The solution was filtered and the purple complex was precipitated from the filtrate by adding alcohol. The compound is soluble in DMSO, alcohol, and acetone.

**Anal.** Calculated for KCo(3-Pr(bi))(1-Pr(bi)H\(_2\)): C, 87.3; C, 35.51; H, 5.98; N, 24.92. Found: Co, 8.5; C, 35.2; H, 6.1; N, 25.0.

In such a solution excess CoCl\(_2\)-6H\(_2\)O 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.** Calculated for KCo(3-Pr(bi))(1-Pr(bi)H\(_2\)): C, 87.3; 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-alkyl(bi))(1-alkyl(bi)H\(_2\))\(_2\) could be prepared.

**KCo(3-Pr(bi))(1-Pr(bi)H\(_2\)).** When the method of Weith\(^6\) for the preparation of 3-phenylbiuret is used for the preparation of alkylbiurets, a mixture of 1-alkylbiuret and 3-alkylbiuret is always obtained.

When a mixture of 0.1 mol of very dry propyleurea and 0.1 mol of PCl\(_3\) is refluxed during 4 hr, a acid solution containing 1-propylbiuret and 3-propylbiuret is obtained after hydrolysis of the reaction mixture with ice. In such a solution excess CoCl\(_2\)-6H\(_2\)O 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 of 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.** Calculated for KCo(en(bi)\(_2\)): C, 31.1; H, 5.59. Found: C, 30.9; H, 5.9.

Bu\(_4\)NCo(en(bi)\(_2\)). Ethylenebis(biuret) (1.2 g) was 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 of the red complex was filtered off and washed with alcohol and ether. 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 excess of alcohol. The precipitate was filtered off and washed with chloroform.

**Anal.** Calculated for KCo(en(bi)\(_2\)): C, 21.6; H, 2.46; N, 25.7. Found: C, 22.0; H, 2.7; N, 25.0.

KCo(3-Ph(bi))(1-Pr(bi)H\(_2\)). (0.85 g) were dissolved in 60 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 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.** Calculated for KCo(3-Ph(bi))(1-Pr(bi)H\(_2\)): C, 32.09; H, 2.15; N, 22.46. Found: C, 31.6; H, 2.3; N, 22.1.

Bu\(_4\)NCo(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% Bu\(_4\)NOH solution in water were added and the resulting blue slurry was oxidized with air during 12 hr.
The precipitate of the crude red complex was then filtered off. It was dissolved in DMSO, the solution was filtered, and the complex was precipitated by adding chloroform and ether. When 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. In 15 ml of DMSO, CoCl₂-6H₂O and o-phenylenebis(biuret) (0.5 g) were dissolved and 5 ml of a 40% Bu₄NOH solution in water was added. Then, with stirring, 15 ml of DMSO, CoCl₂-6H₂O (0.5 g) and o-phenylenebis(biuret) (0.56 g) were dissolved and 5 ml of a 40% Bu₄NOH solution in water was added. Then, with stirring, water (15 ml) was added to the mixture and the resulting slurry was 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 when chloroform was added to this solution.

**Results and Discussion**

Paramagnetic compounds containing Co(III) are coordinated with four atoms in an essentially planar geometry are very rare. Except for some cobalt(III) dithiolate complexes no good examples are known. Apparently the electron-donating capacity of the biuretato and the dithiolato ligands is rare. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known. Except for some cobalt(III) dithiolate complexes no good examples are known.

These complexes could be studied in solutions of rather weak electron-donating solvents such as alcohol, DMSO, and acetone, as they do not take up weak electron donors as further ligands. The magnetic moments of KCo(3-Pr(bi))₂(1-Pr(bi)H₂)₂ in DMSO solution indicate that the triplet ground state is not affected and the positions of the uv-vis absorption bands of KCo(3-Pr(bi))₂(1-Pr(bi)H₂)₂ measured in DMSO, alcohol, and the solid compound are quite the same, indicating that the solvent molecules are not interacting with the planar CoN₄ species.
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>10Dq, 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>

Figure 2. Electronic spectrum of KCo(3-Pr(bi))$_2$(C$_3$H$_7$NH$_2$)$_2$ in ethanol.

Figure 3. Plot of $1/\chi_M$ vs. $T$ of KCo(3-Pr(bi))$_2$2H$_2$O (corrected for diamagnetism).

When excess of an amine is added to an alcoholic solution of these paramagnetic cobalt complexes, diamagnetic six-coordinated adducts are formed. 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° 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°. The susceptibility of KCo(3-Pr(bi))$_2$2H$_2$O has been measured from 6.45 to 300°K. Below 40°K 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.

Writing square root terms of the type

$$\frac{1}{2}\sqrt{(D + E)^2 + 4g_x^2B^2H_z^2}$$

as $[(D + E)/2] + [g_x^2B^2H_z^2/(D + E)]$, 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

$$\chi_M = \frac{N\Sigma_n\left[U_n(1)^2 - 2U_n(2)\right]}{kT} \exp\left(-\frac{U_n(0)}{kT}\right)$$

it is possible to write down expressions for $\chi_M$, $\chi_M_x$, and $\chi_M_x$ (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

$$\chi_M = \frac{\chi_M_x + \chi_M_y + \chi_M_z}{3}$$

This results in

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

$$\chi_M = \frac{2N\beta^2}{3(3kT - 2D)}(\frac{g_x^2}{D + E} + \frac{g_y^2}{D - E})$$

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

$$D = 81.4 \times 10^{-16} \text{erg} = 40.9 \text{cm}^{-1}$$

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

$$\chi_M = \frac{2N\beta^2}{3}(\frac{g_x^2}{D + E} + \frac{g_y^2}{D - E})$$

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

Extended Hückel 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., as diagonal elements

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

in the Hamiltonian matrix and using the Wolfsberg-Helmholz approximation for the estimation of $\chi_M_x$.
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)₄⁺ ion was calculated using interatomic distances as in the alkyl-substituted complex. Assuming D₂h 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 Wolfslberg-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 dₓz and dₓ²−z² orbitals have almost the same energy for all values of K (see Table III). The configuration (dₓz)²(dₓ²−z²)¹ is in excellent agreement with the observed magnetic triplet ground state which is retained even at temperatures as low as 6°K. The calculated d-orbital sequence is the same as found by Figuie 4. Axis system chosen for the extended Huckel calculations.

Figure 4. Axis system chosen for the extended Huckel calculations.

The off-diagonal elements (a₀ₙ[Hₐₙ])/[(Hᵤᵤ + Hᵢᵢ)/2]ΣₖₖK. 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. Theoretical value: (R/T) ln 9. At 20° this value is 55.5 mV for a reversible one-electron transfer.

transferred through the delocalized π-electron system up to the cobalt atom (see Table V). The influence of a π-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.

As the molecular orbitals in which the unpaired electrons are present have xz and x²−y² symmetry, the electronic ground state in D₂h symmetry is 3B₂g. All compounds have D₂h symmetry except the o-phenylenebis(biuret) and the ethylenebis(biuret) complex. In the latter no extensive delocalization over the ethylene bridge is possible. In the o-phenylenebis(biuret) complex the zz molecular orbital, consisting of the Co 3dₓz atomic orbital and all ligand px 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.

Conclusions

The paramagnetic (S = 1) cobalt(III)-bis(biuretato) complexes show a normal Curie-Weiss magnetic behavior from room temperature down to −150°. 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 3dₓz and 3dₓ²−y² atomic orbitals. The polarographic half-wave po-

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 Wolfslberg-Helmholz Parameter K

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<tbody>
<tr>
<td>K = 2.50</td>
<td>dₓ</td>
<td>0.93382</td>
<td>−4.01319</td>
<td>dₓ</td>
<td>0.99451</td>
<td>−8.05548</td>
</tr>
<tr>
<td></td>
<td>dₓ²−z²</td>
<td>0.93514</td>
<td>−9.13753</td>
<td>dₓ²−z²</td>
<td>0.93588</td>
<td>−11.68261</td>
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<tr>
<td></td>
<td>dₓz</td>
<td>0.98489</td>
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<tr>
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<td>dᵧ</td>
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<tr>
<td></td>
<td>dx</td>
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<td>−0.92295</td>
<td>−11.85399</td>
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Table IV. Coefficients of pₓ Atomic Orbitals of Ligand Atoms in the MO that Largely Consists of Co 3dₓz

<table>
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<tbody>
<tr>
<td>K = 2.50</td>
<td>0.98489</td>
<td>0.98419</td>
<td>0.98145</td>
<td>0.08416</td>
<td>0.08792</td>
<td>0.10043</td>
<td>0.05172</td>
<td>0.09438</td>
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<tr>
<td>K = 2.00</td>
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<td>0.98145</td>
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<td>0.09438</td>
<td>0.03690</td>
<td>0.04716</td>
<td>0.04549</td>
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<tr>
<td>K = 1.75</td>
<td>0.98145</td>
<td>0.08416</td>
<td>0.08792</td>
<td>0.10043</td>
<td>0.05172</td>
<td>0.09438</td>
<td>0.03690</td>
<td>0.04716</td>
<td>0.04549</td>
<td>0.04324</td>
</tr>
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</table>

Table V. Polarographic Data\(^a\)

<table>
<thead>
<tr>
<th>Compd</th>
<th>E₁/₂, V</th>
<th>(E_{1/4} - E_{1/2}), b, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCo(3-Ph(bi))₂·2H₂O</td>
<td>−0.71</td>
<td>60</td>
</tr>
<tr>
<td>KCo(3-Ph(bi))₂·2DMSO</td>
<td>−0.64</td>
<td>58</td>
</tr>
<tr>
<td>Bu₄NCo(bi)₃</td>
<td>−0.65</td>
<td>64</td>
</tr>
<tr>
<td>Bu₄NCo(en(bi))₂</td>
<td>−0.63</td>
<td>60</td>
</tr>
<tr>
<td>KCo(o-phen(bi))₃</td>
<td>−0.47</td>
<td>60</td>
</tr>
</tbody>
</table>

\(^a\) All potentials were measured with 0.1 N Bu₄NClO₄ as supporting electrolyte. All waves were of the reduction type.

\(^b\) Theoretical value: (R/T) ln 9.
The Ni(II)-DPAP Reaction

Inorganic Chemistry, Vol. 12, No. 6, 1973

Potentials are dependent on the nature of substituents on the biuret ligand probably due to electron donating or withdrawing through the delocalized \( \pi \)-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\(_4\)NCo(3-Ph(bi))\(_2\), 38637-48-8; Bu\(_4\)NCo(bi)\(_2\) · H\(_2\)O, 38637-49-9; KCo(3-Pr(bi))\(_2\) · (1-Pr(bi)H\(_2\))\(_2\), 36472-84-1; KCo(3-Pr(bi))\(_2\) · 2H\(_2\)O, 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\(_4\)NCo(en(bi))\(_2\), 38637-55-7; Bu\(_4\)NCo(o-phen(bi))\(_2\) · CHCl\(_3\), 38637-56-8; KCo(3-Pr(bi))\(_2\) · (NH\(_3\))\(_2\), 31282-33-4; KCo(3-Pr(bi))(C\(_3\)H\(_7\))NH\(_2\))\(_2\), 31282-34-5; KCo(3-Pr(bi))(pyrrolidine)\(_2\), 31249-56-6; KCo(3-Pr(bi))(pyridine)\(_2\), 31240-71-8.

Acknowledgment. The investigations were supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research. We wish to thank Mr. J. Diersmann for performing the analyses, Dr. C. P. Keijzers for providing the computer program for the Huckel calculations, and Professor L. L. van Reijen for giving us the opportunity to perform magnetic measurements below 150°K. We thank Dr. P. van der Put for help with the interpretation of magnetic data.