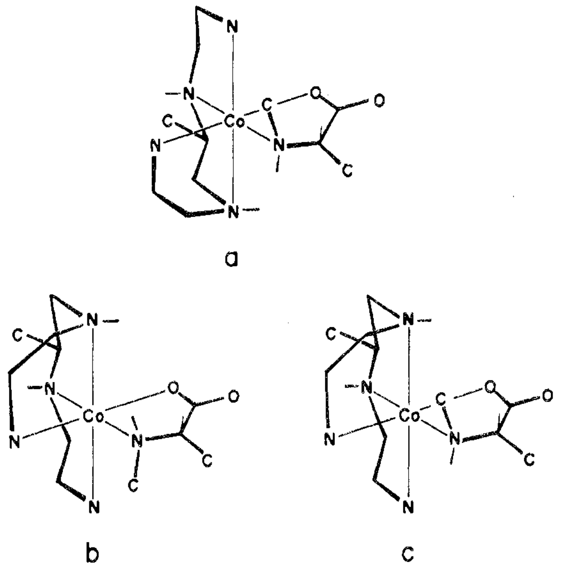

Figure 5. Probable structures of (a) Λ-β_2-(*SSR*)-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$, (b) Δ-β_2-(*RRS*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$, and (c) Δ-β_2-(*RRR*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$.

vanish, though unfavorable steric interactions between the *N*-methyl group and the adjacent trien chelate ring must appear instead of interactions between *N*- and *C*-methyl groups. The pmr results of Δ-β_2-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ suggest that the Δ-β_2-*RRR* configuration has approximately equal stabilities as compared with the Δ-β_2-*RRS* configuration.

The Δ-β_2-*RSS* configuration, alternative to the Δ-β_2-*RRR* form, has been shown to be less stable than the Δ-β_2-*RRS* form in terms of 3.2 kcal/mol.[7] It seems to be rather unlikely that the Δ-β_2-*RSS* and Δ-β_2-*RRS* isomers have comparable stabilities, even if the entropy term affects appreciably the free-energy difference. We concluded, therefore, that the Δ-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion, as well as the Δ-β_2-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion, adopts the *RRS* and *RRR* configurations at equilibrium. The probable structures for 5(*S*)-metrien complexes are illustrated in Figure 5, along with that for the 5(*R*)-metrien complex.

Table I. Assignments of *C*- and *N*-Methyl Proton Resonances[a] of *N*-Me-(*S*)-ala Complexes

	C–CH$_3$ (5-metrien)	C–CH$_3$ (*N*-Me-(*S*)-ala)	N–CH$_3$
Λ-β_2-(*SSR*)-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$	1.37	1.53	2.61
Δ-β_2-(*RRS*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$	1.34	1.42	2.38
Δ-β_2-(*RRR*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$	1.34	1.50	2.58

[a] Parts per million from DSS.

It is somewhat difficult to assign individual species for the *RRS* and *RRR* configurations. The only remarkable difference between these isomers is the relative orientations of the *N*- and *C*-methyl groups. The pmr signals of the *N*-methyl groups were observed at 2.58 and 2.38 ppm for an isomeric mixture of the 5(*S*)-metrien complex (Figure 2c). The corresponding signal for the Λ-β_2-(*SSR*)-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion was observed at 2.61 ppm. We assign here the *N*-methyl signal at 2.38 ppm, apart from the other signals, for that with the *S* (cis) configuration. Then, the signal at 2.58 ppm for the 5(*S*)-metrien complex and that at 2.61 ppm for the 5(*R*)-metrien complex are simultaneously assigned to the *R* (trans) configuration. The assignments of pmr signals are summarized in Table I.

In order to confirm the conclusions in this study, we have examined *N*-methyl-(*S*)- and *N*-methyl-(*R*)-alaninatocobalt(III) complexes with *N*,*N*′-bis(β-aminoethyl)-(1*R*,2*R*)-diaminocyclohexane. The trien derivative employed here has no possibility of conformational inversion at the central diamine linkage. The results on these systems will be reported in a subsequent paper.

Registry No. Λ-β_2-[Co[5(*R*)-metrien](*N*-Me-(*S*)-ala)](ClO$_4$)$_2$, 38671-62-4; Δ-β_2-[Co[5(*S*)-metrien](*N*-Me-(*S*)-ala)](ClO$_4$)$_2$, 38671-64-6; Δ-β_2-[Co[5(*S*)-metrien](*N*-Me-(*S*)-ala]I$_2$, 38671-65-7; Δ-β_2-[Co[5-(*S*)-metrien](*N*-Me-(*S*)-ala)]$^{2-}$, 38671-66-8.

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Spin-Triplet Cobalt Complexes of Biuret and Related Ligands

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A number of planar Co^{III}N$_4$ 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 Huckel calculations. The d_{xz} and $d_{x^2-y^2}$ 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-

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(1) J. J. Bour and J. J. Steggerda, *Chem. Commun.*, 85 (1967).

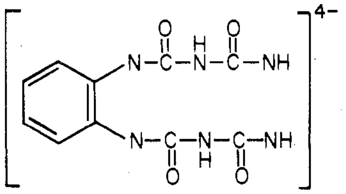
(2) J. J. Bour, P. J. M. W. L. Birker, and J. J. Steggerda, *Inorg. Chem.*, **10**, 1202 (1971).

ate(III) ion could be synthesized having a spin-triplet ground state.[1,3] The crystal structure of the 3-*n*-propyl-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.

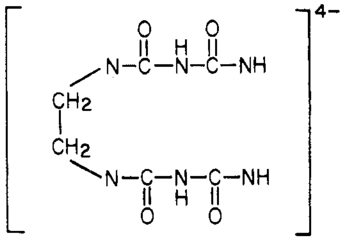
Experimental Part

Abbreviations. Abbreviations used in this paper are as follows: bi = $[HNCONHCONH]^{2-}$, 3-Ph(bi) = $[HNCON(C_6H_5)CONH]^{2-}$, 3-Pr(bi) = $[HNCON(C_3H_7)CONH]^{2-}$, 1-Pr(bi)H_2 = $H_2NCONHCONHC_3H_7$

o-phen(bi)$_2$ =



(en)bi$_2$ =



DMSO = dimethyl sulfoxide and Bu_4NOH = tetra-*n*-butylammonium hydroxide.

Syntheses. *o*-Phenylenebis(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 (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. Calcd for KCo(bi)$_2$: K, 13.03; Co, 19.65; C, 16.00; H, 2.00; N, 28.00. Found: K, 13.4; Co, 19.3; C, 15.7; H, 2.2; N, 27.2.

KCo(3-Ph(bi))$_2$·2DMSO. 3-Phenylbiuret was prepared according to Weith.[6] $CoCl_2 \cdot 6H_2O$ (2.4 g) and 3-phenylbiuret (5.1 g) were dissolved in 100 ml of water. KOH (3.6 g dissolved in 5 ml of water) was added to this solution. The resulting blue slurry was oxidized with air during 24 hr. Then the insoluble material was removed by filtration. To the red filtrate about the same volume of alcohol was added and then sufficient ether was added to form red and colorless liquid layers. The upper colorless layer was removed, alcohol and ether again were added, and the same procedure was repeated several times until finally a red precipitate was obtained. This precipitate was dissolved in DMSO. Within a few minutes the color of the solution turned from red to yellow. The solution was filtered and the yellow complex was precipitated by adding chloroform and ether. It was filtered off in dry air and washed with chloroform and ether. It is soluble in acetone, alcohol, and DMSO.

Anal. Calcd for KCo(3-Ph(bi))$_2$·2DMSO: Co, 9.8; C, 39.6; H, 4.28; N, 13.8. Found: Co, 9.3; C, 39.4; H, 4.25; N, 13.5.

Bu_4NCo(3-Ph(bi))$_2$. $CoCl_2 \cdot 6H_2O$ (0.8 g) and 3-phenylbiuret (1.7 g) were dissolved in 100 ml of water. A 40-ml sample of a 40% Bu_4NOH solution in water was added and the resulting mixture was oxidized with air during 24 hr. Then the insoluble material was filtered off and the red filtrate was concentrated as described above with alcohol and ether finally yielding a red precipitate, that was dissolved in DMSO. Dropwise aqueous 1 *N* HCl was added to this red 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. Calcd for Bu_4NCo(3-Ph(bi))$_2$: C, 58.61; H, 7.69; N, 14.95. Found: C, 58.2; H, 7.7; N, 14.9.

Bu_4NCo(bi)$_2$·H_2O. $CoCl_2 \cdot 6H_2O$ (5 g) was dissolved in 200 ml of water. Biuret (6 g) and 75 ml of a 40% Bu_4NOH solution in water were added. The resulting mixture was oxidized 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. Calcd for Bu_4NCo(bi)$_2$·H_2O: C, 46.0; H, 8.4; N, 18.8. Found: C, 45.6; H, 7.9; N, 18.8.

KCo(3-Pr(bi))$_2$(1-Pr(bi)H_2)$_2$. 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. So when a mixture of 0.1 mol of very dry propylurea 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 $CoCl_2 \cdot 6H_2O$ 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. Calcd for KCo(3-Pr(bi))$_2$(1-Pr(bi)H_2)$_2$: Co, 8.73; C, 35.31; 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))$_2$(1-alkyl(bi)H_2)$_2$ could be prepared.

KCo(3-Pr(bi))$_2$·2H_2O. From a solution of KCo(3-Pr(bi))$_2$(1-Pr(bi)H_2)$_2$ in moist DMSO the compound KCo(3-Pr(bi))$_2$·2H_2O precipitated upon addition of chloroform and ether. It was filtered off and washed with chloroform.

Anal. Calcd for KCo(3-Pr(bi))$_2$·2H_2O: 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)H_2)$_2$ 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. Calcd 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 of the red complex was then 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. Calcd 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)$_2$). $CoCl_2 \cdot 6H_2O$ (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. Calcd 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.

Bu_4NCo(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_4NOH solution in water were added and the resulting blue slurry was oxidized with air during 12 hr.

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[3] J. J. Steggerda and J. J. Bour, *Proc. Symp. Coord. Chem.*, 274 (1970).

[4] J. J. Bour, P. T. Beurskens, and J. J. Steggerda, *J. Chem. Soc., Chem. Commun.*, 221 (1972).

[5] T. L. Davis and K. C. Blanchard, *J. Amer. Chem. Soc.*, **51**, 1804 (1929).

[6] W. Weith, *Ber.*, **10**, 1744 (1877).

Table I. Spectral and Magnetic Data of Triplet Cobalt Complexes

	Magnetic properties[a]			Uv-vis spectral data[b]			
Compd	μ_{eff},[c] BM	Measd temp range over which Curie-Weiss law is obeyed, °C	Θ, °C	ν_3, kK	ν_2, kK	ν_1, kK	Solvent
$KCo(bi)_2$	3.4	−150 to +100	0	13.2	12.7	11.2	Solid KBr
$Bu_4NCo(bi)_2$				13.3 sh	12.6 (100)	11.6 (50)	C_2H_5OH
				13.2	12.8	11.5	DMSO
$KCo(3\text{-}Pr(bi))_2(1\text{-}Pr(bi)H_2)_2$	3.3	−150 to +20	−16	13.4 sh	12.8 (107)	11.5 (51)	DMSO
	3.4 (DMSO)			13.4	12.8	11.5	C_2H_5OH
				13.7	13.3	11.4	Solid KBr
$KCo(3\text{-}Pr(bi))_2\cdot 2DMSO$	3.5	−150 to +20	*d*				
$KCo(3\text{-}Pr(bi))_2\cdot 2H_2O$	3.4	−250 to +20	−19		13.1 (100)	11.4 (50)	DMSO
	3.5 (DMSO)						
$KCo(3\text{-}Ph(bi))_2\cdot 2DMSO$	3.5	−150 to +20	*d*		12.8	11.1	C_2H_5OH
$Bu_4NCo(en(bi)_2)$	3.3	−150 to +20	−20	13.0 (140)	12.2 sh	11.5 (40)	DMSO
$KCo(o\text{-}phen(bi)_2)$	3.1			13.8 (1240)		11.2 (600)	DMSO
$Bu_4NCo(o\text{-}phen(bi)_2)\cdot CHCl_3$	3.4	−150 to +20	−20	13.8 (1200)		11.2 (600)	DMSO

[a] Corrections for diamagnetism taken from J. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Part I, Vol. 4, Interscience, New York, N. Y., 1963, pp 1778–1781. [b] Only bands with small extinction coefficients given. Extinction coefficients in parentheses. [c] At room temperature. Measured on solid samples, unless solvent is indicated. [d] Not exactly determined due to inaccuracy in measurement.

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.

Anal. Calcd for $Bu_4NCo(en(bi)_2)$: C, 49.90; H, 8.38; N, 18.51. Found: C, 48.1; H, 8.3; N, 18.8.

$Bu_4NCo(o\text{-}phen(bi)_2)\cdot CHCl_3$. In 15 ml of DMSO, $CoCl_2\cdot 6H_2O$ (0.5 g) and *o*-phenylenebis(biuret) (0.56 g) were dissolved and 5 ml of a 40% Bu_4NOH 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.

Anal. Calcd for $Bu_4NCo(o\text{-}phen(bi)_2)\cdot CHCl_3$: C, 46.6; H, 6.2; N, 14.09. Found: C, 46.3; H, 6.3; N, 14.13.

The presence of chloroform was confirmed by the mass spectrum of the compound at 120°.

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

Physical Measurements. Magnetic susceptibilities were measured with 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 standard PAR temperature control unit was used in the temperature range of 4.2–120°K. The temperatures in this range were calculated from the magnetic susceptibility of a sample of $KCr(SO_4)_2\cdot 12H_2O$.[7] The field strength was 16563 G. Polarographic data were obtained with a Metrohm Polarecord E261. Dry vacuum-distilled DMSO was used as solvent with 0.1 *M* Bu_4NClO_4 as supporting electrolyte. A dropping mercury electrode was used *vs.* a saturated calomel electrode. Ultraviolet and visible spectra were measured with a Unicam SP 700C; transmission spectra were measured in solid KBr with a Cary Model 14.

Results and Discussion

Paramagnetic compounds in which Co(III) is 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 so strong that the relatively large electron density on the central cobalt atom makes coordination of strong electron-donating ligands (*e.g.*, amines) unfavorable, while there is in the case of the biuretato complexes no indication of coordination with weak electron donors (*e.g.*, H_2O, DMSO, alcohol). Sometimes, however, the solid compounds contain DMSO, H_2O, or 1-alkylbiuret. It has been shown by crystallographic structure determination[4] 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 $[K(1\text{-alkyl(bi)}H_2)_2][Co(3\text{-alkyl(bi)})_2]$. 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 CoN_4 complexes that are soluble in water (*e.g.*, $KCo(3\text{-}Pr(bi))_2\cdot 2DMSO$) 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 H_2O 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).

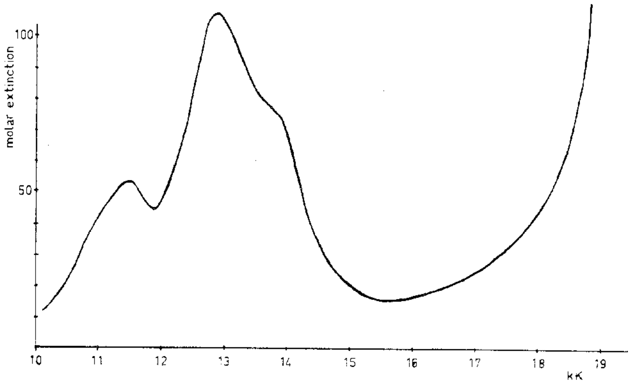

Figure 1. Electronic spectrum of $KCo(3\text{-}Pr(bi))_2(1\text{-}Pr(bi)H_2)_2$ in DMSO.

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 $KCo(3\text{-}Pr(bi))_2\cdot 2H_2O$ and $KCo(3\text{-}Pr(bi))_2(1\text{-}Pr(bi)H_2)_2$ in DMSO solution indicate that the triplet ground state is not affected and the positions of the uv-vis absorption bands of $KCo(3\text{-}Pr(bi))_2(1\text{-}Pr(bi)H_2)_2$ measured in DMSO, alcohol, and the solid compound are quite the same, indicating that the solvent molecules are not interacting with the planar CoN_4 species.

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(7) C. M. Herzfeld, "Temperature. Its Measurement and Control in Science and Industry," Vol. 3, Part 1, Reinhold, London, 1962, p 83.

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

Compd	ν_1, kK	ν_2, kK	10*Dq*, kK	*B*, K
$Co(3\text{-}Pr(bi))_2(NH_3)_2^-$	20.4 (70)	27.4 sh	21.4	500
$Co(3\text{-}Pr(bi))_2(C_3H_7NH_2)_2^-$	18.5 (45)	27.8 sh	19.0	730
$Co(3\text{-}Pr(bi))_2(\text{pyrrolidine})_2^-$	17.4 (42)			
$Co(3\text{-}Pr(bi))_2(py)_2^-$	18.2 (47)			

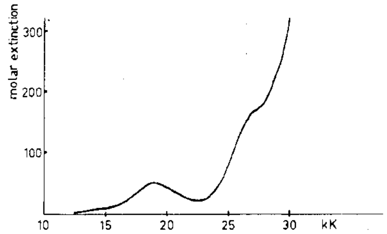

Figure 2. Electronic spectrum of $KCo(3\text{-}Pr(bi))_2(C_3H_7NH_2)_2$ in ethanol.

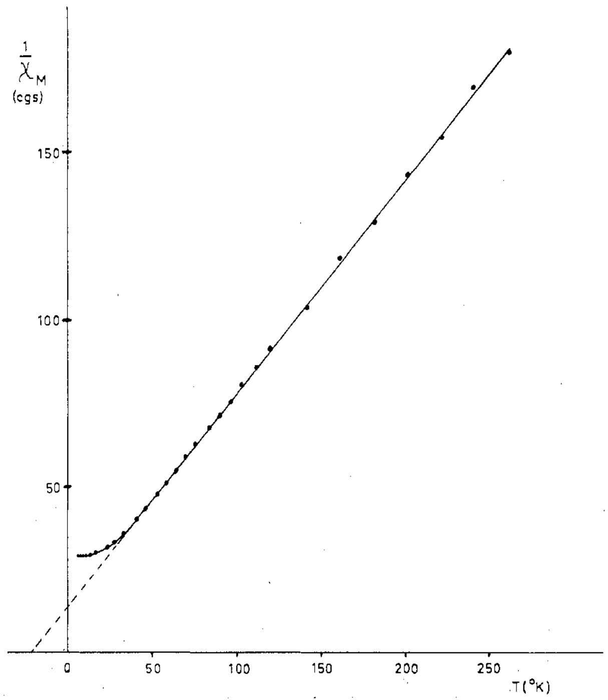

Figure 3. Plot of $1/\chi_M$ *vs.* T of $KCo(3\text{-}Pr(bi))_2 \cdot 2H_2O$ (corrected for diamagnetism).

When excess of an amine is added to an alcoholic solution of these paramagnetic cobalt complexes, diamagnetic six-coordinated adducts are formed.[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° and the parent four-coordinated paramagnetic complex is left. The uv-vis spectra of these CoN_4L_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 $KCo(3\text{-}Pr(bi))_2 \cdot 2H_2O$ 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.[8]

Writing square root terms of the type $^1/_2\sqrt{(D+E)^2 + 4{g_x}^2\beta^2{H_x}^2}$ as $\simeq[(D+E)/2] + [{g_x}^2\beta^2{H_x}^2/(D+E)]$, 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[9]

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

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

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

it is possible to write down expressions for χ_{M_x}, χ_{M_y}, and χ_{M_z} (*i.e.*, χ_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

$$\chi_M = \frac{N\beta^2}{3\left(1 + \exp\left(-\frac{D+E}{kT}\right) + \exp\left(-\frac{D-E}{kT}\right)\right)}\left[\frac{{g_z}^2}{E} \times \left(\exp\left(-\frac{D-E}{kT}\right) - \exp\left(-\frac{D+E}{kT}\right)\right) + \frac{2{g_x}^2}{D+E}\left(1 - \exp\left(-\frac{D+E}{kT}\right)\right) + \frac{2{g_y}^2}{D-E}\left(1 - \exp\left(-\frac{D-E}{kT}\right)\right)\right]$$

At low temperatures this expression for χ_M approximates

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

This means that at low temperatures χ 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 χ_M approximates

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

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 $H_{ii} = \langle ao_i|H|ao_i\rangle$ in the Hamiltonian matrix and using the Wolfsberg-Helmholz[12] approximation for the estimation of

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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 Wolfsberg-Helmholz Parameter *K*

	$K = 2.50$		$K = 2.00$		$K = 1.75$	
	Coeff	Energy, eV	Coeff	Energy, eV	Coeff	Energy, eV
d_{xy}	0.93382	−4.01319	0.94451	−8.05548	−0.94919	−10.86347
$d_{x^2-y^2}$	−0.95914	−9.13753	−0.93858	−11.68261	−0.90342	−13.76943
d_{xz}	0.98489	−9.13893	0.98419	−11.68973	−0.98145	−13.76865
d_{yz}	0.97602	−9.30084	−0.97604	−11.80467	−0.97741	−13.84998
d_{z^2}	0.94288	−9.36949	−0.92295	−11.83599	−0.88887	−13.87696

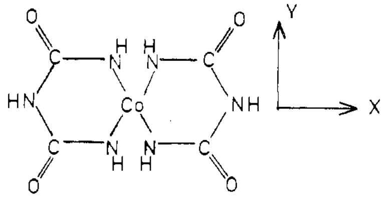
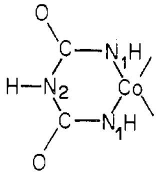


Figure 4. Axis system chosen for the extended Huckel calculations.

Table IV. Coefficients of p_z Atomic Orbitals of Ligand Atoms in the MO that Largely Consists of Co $3d_{xz}$



	$K = 2.50$	$K = 2.00$	$K = 1.75$
Co d_{xz}	0.98489	0.98419	0.98145
N_1 p_z	0.08416	0.08792	0.10043
C p_z	0.05172	0.04938	0.03690
O p_z	0.04716	0.04549	0.04324
N_2 p_z	0.08425	0.08744	0.09744

Table V. Polarographic Data[a]

Compd	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$,[b] mV
$KCo(3\text{-}Pr(bi))_2 \cdot 2H_2O$	−0.71	60
$KCo(3\text{-}Ph(bi))_2 \cdot 2DMSO$	−0.64	58
$Bu_4NCo(bi)_2$	−0.65	64
$Bu_4NCo(en(bi)_2)$	−0.63	60
$KCo(o\text{-}phen(bi)_2)$	−0.47	60

[a] All potentials were measured with 0.1 *N* Bu_4NClO_4 as supporting electrolyte. All waves were of the reduction type. [b] Theoretical value: (RT/nF) ln 9. At 20° this value is 55.5 mV for a reversible one-electron transfer.

the off-diagonal elements $\langle ao_i|H|ao_j\rangle = [(H_{ii} + H_{jj})/2]\, S_{ij}K$. Atomic orbitals were described by single-ζ Slater-type orbitals for s and p orbitals with ζ values taken from Clementi and Raimondi[13] and from Richardson, *et al.*,[14] and double-ζ functions were used for the description of the Co 3d orbitals taken from Richardson, *et al.*[15] The MO diagram of the unsubstituted $Co(bi)_2^-$ ion was calculated using interatomic distances as in the alkyl-substituted complex.[4] 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 Wolfsberg-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 $d_{x^2-y^2}$ orbitals have almost the same energy for all values of *K* (see Table III). The configuration $(d_{xz})^1(d_{x^2-y^2})^1$ 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 Shupack, *et al.*,[16] for $Ni(mnt)_2^{2-}$ and used by Baker-Hawkes, *et al.*,[17] to explain the paramagnetism of $Co(tdt)_2^-$.

One of the molecular orbitals which is occupied by an unpaired electron has *xz* symmetry. It is largely built up from the Co d_{xz} atomic orbital but there is also a contribution from all the p_z orbitals of the ligand atoms. The p_z orbital of the nitrogen atom on the 3 position has a coefficient of about 0.1 (see Table IV). In view of this fact it is not surprising that the value of the polarographic half-wave potential is in part determined by the nature of the substituent on the remote 3 position as its influence can be 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 $x^2 - y^2$ symmetry, the electronic ground state in D_{2h} symmetry is $^3B_{2g}$. All compounds have D_{2h} 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 *xz* molecular orbital, consisting of the Co $3d_{xz}$ atomic orbital and all ligand p_z 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 $3d_{xz}$ and $3d_{x^2-y^2}$ 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 withdrawing through the delocalized π-electron system which overlaps with the Co $3d_{xz}$ orbital.

Registry No. $KCo(bi)_2$, 38637-46-6; $KCo(3\text{-}Ph(bi))_2 \cdot 2DMSO$, 38637-47-7; $Bu_4NCo(3\text{-}Ph(bi))_2$, 38637-48-8; $Bu_4NCo(bi)_2 \cdot H_2O$, 38637-49-9; $KCo(3\text{-}Pr(bi))_2(1\text{-}Pr(bi)H_2)_2$, 36472-84-1; $KCo(3\text{-}Pr(bi))_2 \cdot 2H_2O$, 38637-51-3; $KCo(3\text{-}Pr(bi))_2 \cdot 2DMSO$, 38637-52-4; $KCo(en(bi)_2)$, 38637-53-5; $KCo(o\text{-}phen(bi)_2)$, 38637-54-6; $Bu_4NCo(en(bi)_2)$, 38637-55-7; $Bu_4NCo(o\text{-}phen(bi)_2) \cdot CHCl_3$, 38637-56-8; $KCo(3\text{-}Pr(bi))_2(NH_3)_2$, 31282-33-4; $KCo(3\text{-}Pr(bi))_2(C_3H_7NH_2)_2$, 31282-34-5; $KCo(3\text{-}Pr(bi))_2(pyrrolidine)_2$, 31249-56-6; $KCo(3\text{-}Pr(bi))_2(pyridine)_2$, 31240-71-8.

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Kinetics of the Nickel(II)-2-(4-Dimethylaminophenylazo)pyridine Reaction in Pyridine and in Pyridine-Nitromethane

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The following reaction between nickel(II) and 2-(4-dimethylaminophenylazo)pyridine (DPAP) in pyridine and in pyridine-nitromethane solvents has been studied

$$Ni^{2+} + DPAP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiDPAP^{2+}$$

The rate constants (25°) and activation parameters in various solvents are as follows (solvent, k_3, $\Delta H_3^{\ddagger}$, $\Delta S_3^{\ddagger}$, k_{-3}, $\Delta H_{-3}^{\ddagger}$, $\Delta S_{-3}^{\ddagger}$): pyridine, $1.7 \times 10^4\ M^{-1}\ sec^{-1}$, 13.7 kcal/mol, 6 eu, 12 sec^{-1}, 15 kcal/mol, −4 eu; 6.20 M pyridine in nitromethane, $5.0 \times 10^3\ M^{-1}\ sec^{-1}$, 11.1 kcal/mol, −4 eu, 20 sec^{-1}, 10 kcal/mol, −21 eu; 0.125 M pyridine in nitromethane, $3.5 \times 10^5\ M^{-1}\ sec^{-1}$, 9 kcal/mol, −3 eu, · · ·, · · ·, · · ·. The data are consistent with either the Bennetto-Caldin or Eigen-Wilkins mechanisms but not with a mechanism involving a reactive five-coordinate intermediate.

Introduction

Nickel(II) complexation reactions in aqueous solutions have been widely studied. Two review articles by Kustin and Swinehart[1] and by Wilkins[2] summarize the available data for these reactions. The mechanism for these reactions can be written as

$$Ni(H_2O)_6{}^{2+} + L^{n-} \overset{K_1}{\rightleftharpoons} Ni(H_2O)_6{}^{2+},L^{n-} \qquad (1)$$

$$Ni(H_2O)_6{}^{2+},L^{n-} \xrightarrow{k_1} Ni(H_2O)_{6-p}L^{2-n} + pH_2O$$

where $Ni(H_2O)_6{}^{2+},L^{n-}$ is an ion pair. The ion pairing constant K_1 can be calculated from an equation derived by Fuoss[3] and by Eigen.[4] Since temperature-jump and stopped-flow kinetic experiments provide data for the product K_1k_1, k_1 can be determined. When L^{n-} is a water molecule, mechanism 1 becomes the generalized equation for solvent exchange

$$Ni(H_2O)_6{}^{2+} + H_2O^* \overset{k_2}{\rightleftharpoons} Ni(H_2O)_5(H_2O^*)^{2+} + H_2O \qquad (2)$$

Nmr line broadening studies have been used to determine the value of k_2 in the above reaction.[5] In many Ni(II) aqueous complexation reactions,[2] k_1 has been calculated to be approximately equal to k_2. This more than coincidental agreement between k_1 and k_2 has been interpreted to mean that the rate-determining step in mechanism 1 is the elimination of a bonded water molecule from the first solvation sphere of the solvated Ni(II) ion.[1,2]

To determine the effect the solvent has on complexation reactions, these reactions must be studied in different solvents. Until recently, most complexation reactions have been studied in aqueous solvents. Research on nonaqueous complexation reactions has been done in three major areas. Nmr line broadening techniques have been used to determine the rates of solvent exchange for solvated metal cations in both pure- and mixed-solvent systems.[6-29] Nmr techniques have

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