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Deprotonation of Glycine and Iminodiacetic Acid Complexes of Cobalt(III)

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Treatment of tris(glycinato)cobalt(III) and potassium bis(iminodiacetato)cobaltate(III) with potassium amide in liquid ammonia at −33.5° has led to the isolation and characterization of the compounds: $K[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$, $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$, and $K_3[Co(NHCH_2CO_2)_3]$ and $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ and $K_3[Co(N(CH_2CO_2)_2)_2]$. The infrared spectra and magnetic properties of these and the parent complexes have been studied to examine the effect of proton abstraction upon the bonding in these compounds.

Cobalt(III)-ammine and substituted ammine complexes do not, in general, exhibit marked acidic behavior in aqueous solution.[1-4] Studies of the acidic properties in aqueous solution of $[Co(en)_3]I_3$,[1,2] of $[Co(NH_3)_6]I_3$,[1,2] and of some mixed ethylenediamine and ammine–cobalt(III) complexes,[4] such as $[Co(en)_2(OH)_2]^+$, have shown that the dissociation constants of these complexes are $<10^{-12}$ and that proton abstraction from the coordinated amino groups in these complexes could only be achieved under strongly basic conditions. Similar data pertaining to cobalt(III)–amino acid complexes do not, however, appear to be available.

Acid dissociation constants for the protonated and zwitter glycine ions have been determined by Irving and Williams[5] ($pK_{ZH^+} = 2.24$, $pK_{ZH^\pm} = 9.85$) and analogous data for iminodiacetic acid have been published by Chabereck and Martell[6] ($pK_{ZH_2} = 2.54$, $pK_{ZH^-} = 9.12$). In neither case, however, have the acid dissociation data been determined for the removal of a further proton, in this case from the uncharged amino or imino group, probably because this would necessitate measurements at very high pH. Coordination of these ligands to a transition metal ion, particularly to ions of high charge and small radius such as Co(III), should increase the acidity of these protons,[7,8] but it is doubtful whether this increase would be sufficient for these protons to be readily titrated in aqueous solution.

Through the use of solvents more basic than water, we have recently shown,[9] however, that proton abstraction from the coordinated amino group in bis(glycinato)nickel(II) and bis(β-alaninato)nickel(II) may be achieved by titration with solutions of potassium amide in liquid ammonia and that deprotonated derivatives such as $K[Ni(NHCH_2CO_2)(NH_2CH_2CO_2)]$ and $K_2[Ni(NHCH_2CO_2)_2]$ may be isolated from these solutions.

We have since extended this work and here report results from studies of the reactions of tris(glycinato)cobalt(III) and potassium bis(iminodiacetato)cobaltate(III) in liquid ammonia with amide ion and of the products isolated.

Experimental Section

Methods.—Reactions in liquid ammonia and procedures for handling the products thereof were the same as described elsewhere.[10] Air-sensitive products were stored and/or transferred in a drybox containing a helium atmosphere maintained oxygen and water free by continuous exposure to liquid Na–K alloy.

Infrared spectra (Table I) were recorded with Beckman IR-7 and IR-11 instruments. Spectra in the region 600–3800 cm^{-1} were taken as mulls in Nujol and hexachlorobutadiene on NaCl plates. Spectra in the 200–700-cm^{-1} region were recorded using Nujol mulls on CsI plates. Typical spectra are shown in Figure 1.

Magnetic susceptibility measurements were made with a Curie–Cheneveau balance and were corrected for diamagnetic contributions.[11]

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kV and 14 mA. Exposure times were 6–12 hr; relative intensities were estimated visually. The *d* spacings corresponding to the most intense lines (with relative intensities in parentheses) are listed immediately following analytical data.

Carbon, hydrogen, and nitrogen analyses were performed, either in these laboratories using a Coleman Model 33 carbon–hydrogen analyzer and a Coleman Model 29 nitrogen analyzer or by commercial analytical laboratories. Whenever samples contained both cobalt and potassium, standard methods for determining cobalt gravimetrically were found to give inconsistent results, and in these cases, potassium was determined gravimetrically as the tetraphenylborate.[12] In the absence of potassium, cobalt was determined by reduction to the metal in a stream of hydrogen at 700°.

Materials.—Unless otherwise indicated, all chemicals were reagent grade and anhydrous.

***trans*-Tris(glycinato)cobalt(III)**, $[Co(NH_2CH_2CO_2)_3]$, was prepared as described by Mori, *et al.*[13] *Anal.* Calcd for $Co(NH_2CH_2CO_2)_3$: Co, 21.0; C, 25.6. Found: Co, 20.9; C, 25.6. X-Ray diffraction data: 6.75 (1.0), 6.06 (0.5), 4.84 (0.9), 3.76 (0.4), 3.28 (0.5). The product was diamagnetic.

Potassium *trans*-bis(iminodiacetato)cobalt(III), K[Co(NH-

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Table I

Infrared Spectra in the 200–3800-Cm^{-1} Region

$Co(NH_2CH_2CO_2)_3$	$KCo(NH_2CH_2CO_2)_2$-$(NHCO_2)_2$	$K_2Co(NH_2CH_2CO_2)$-$(NHCH_2CO_2)_2$	K_3Co-$(NHCH_2CO_2)_3$	N–H/N–D	Tentative assignments
3315 m	3260 s	3300 m	3300 w	1.36	$\nu(NH)$, $\nu(NH_2)$
3220 s	3150 s	3140 m	3275 w	1.34	
3118 s				1.34	
2965 w	2940 w	2940 w	2935 w		$\nu(CH_2)$
		2850 w, sh	2900 w		
			2860 w		
1635 vs	1612 vs	1592 vs	1583 s		$\nu_a(CO_2)$
		1450 w	1450 m		$\gamma(NH)$
1425 m	1425 m	1420 s	1425 s		$\gamma(CH_2)$
1370 s	1380 s	1395 s	1400 s		$\nu_s(CO_2)$
1330 s	1338 s	1339 s	1340 m		$\omega(CH_2)$
1310 s		1830 m		1.27	$\omega(NH_2)$
1236 w	1215 m	1238 w	1240 w		
1188 m	1195 m	1190 w	1210 w		$\nu(C-N)$
1138 m		1136 w	1140 vw		$\gamma(CH_2)$
1043 w	1043 m	1042 vw		1.30	$\gamma(NH_2)$
950 w	955 w				$\nu(C-C)$
923 m	926 m	914 w	893 m		$\rho(CH_2)$
		892 w			
		855 m	855 m		
818 w				1.21	$\rho(NH_2)$
785 w					
755 w	730 m	723 w	725 w		$\delta(CO_2)$
		664 m	667 m		
610 s	594 s	610 s	599 m		$\rho(CO_2)$
598 s		600 s			
555 m	555 m, sh	555 m			
535 m	538 m, sh	535 m	534 m, sh		$\nu(Co-N)$
509 m	513 m	510 m	508 s		
496 m, sh			492 m		
			472 m, sh		
440 s	442 m	441 m	446 m, sh		$\nu(Co-O)$
413 w, sh	417 w, sh				
365 m	344 w	365 w	365 vw		$\delta(N-Co-N)$
350 m		350 w	350 vw, sh		
284 m	283 m	280 m	282 m, sh		
$KCo(NH(CH_2CO_2)_2)_2$	$K_2Co(NH(CH_2CO_2)_2)$-$(N(CH_2CO_2)_2)$	$K_3Co(N(CH_2CO_2)_2)_2$			
3130 m	3170 w			1.34	$\nu(NH)$
2990 w	2940 m	2950 w			$\nu(CH_2)$
2900 m	2820 w	2820 w			
1652 vs	1605 vs	1595 vs			$\nu_a(CO_2)$
1440 w				1.30	$\delta(NH)$
1368 s	1390 s	1400 s			$\nu_s(CO_2)$
1332 m	1322 m	1320 m			$\omega(CH_2)$
1241 w	1280 m	1276 m			
1135 w	1140 vw	1145 vw			$\nu(C-N)$
1119 m	1115 vw	1118 vw			$\gamma(CH_2)$
1045 w	1039 w	1022 w			
	1023 w				
962 w	964 vw	973 vw			$\nu(C-C)$
	950 vw				
926 m	920 m	912 m			$\rho(CH_2)$
903 m	910 m				
	829 vw	827 w			
787 m	783 vw				$\delta(CO_2)$
768 vw	760 vw				
	719 m	717 m			
623 w	643 w	640 w			$\rho(CO_2)$
610 w	617 m	610 m			
589 w					
571 m	561 m	560 m			$\nu(CO-N)$
555 m	533 m				
538 m					
463 m	464 m				$\nu(Co-O)$
450 m	457 m				
	445 m				
395 w					
368 w	365 w	383 vw			$\delta(N-Co-N)$
362 w					
325 w					

$(CH_2CO_2)_2)_2]$, was prepared by the method of Tsuchida, *et al.*[14] The initial product was converted to the anhydrous material by heating at *ca.* 120° for 2 hr and allowing the product to cool *in vacuo* over KOH pellets. *Anal.* Calcd for $K[Co(NH(CH_2CO_2)_2)_2]$: K, 10.9; C, 26.7. Found: K, 10.8; C, 26.5. X-Ray diffraction data: 8.42 (0.9), 6.94 (0.5), 5.75 (0.6), 5.21 (0.6), 5.03 (1.0), 4.20 (0.8). The product was diamagnetic.

Preliminary Experiments with *trans*-Tris(glycinato)cobalt(III).—To determine whether or not $[Co(NH_2CH_2CO_2)_3]$ undergoes either solvolysis or ligand substitution, a 0.51-g sample was exposed to 50 ml of liquid ammonia at −78° for 3 hr. The resulting purple suspension was separated by filtration and washed twice with 15-ml portions of ammonia. After removal of excess solvent under reduced pressure, the solid product was transferred to the drybox for removal of samples. An X-ray diffraction pattern for this product was identical with that of the starting material. *Anal.* Found: C, 24.9.

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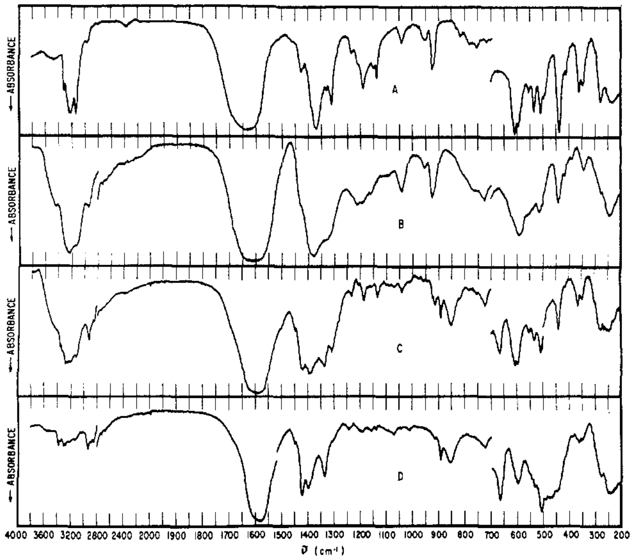

Figure 1.—The infrared spectra of (A) $[Co(NH_2CH_2CO_2)_3]$, (B) $K[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$, (C) $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$, and (D) $K_3[Co(NHCH_2CO_2)_3]$.

To investigate the effect of KNH_2 on ammonia solutions of $[Co(NH_2CH_2CO_2)_3]$, a purple solution of 0.92 g of $[Co(NH_2CH_2CO_2)_3]$ in 100 ml of liquid ammonia was titrated at −33.5° with KNH_2 formed from 0.514 g of potassium in 20 ml of ammonia. Upon addition of 2–3 ml of titrant, a reddish brown solid began to form, and by the time 1 molar equiv of KNH_2 had been added, all of the purple starting material had dissolved. Precipitation was completed by the addition of a second molar equivalent of KNH_2 solution; at this stage the reaction mixture consisted of a colorless supernatant liquid and a brown solid product. The addition of a third molar equivalent of amide solution was marked by a further change in the color of this solid product—from brown to gray. Part of the same product redissolved as more amide was added, to give a blue solution.

Potentiometric measurements were made after the addition of each 0.3-ml portion of the amide solution until all of the titrant had been consumed. A plot of millivolts *vs.* milliliters showed significant inflections at approximately 5.0, 8.7, and 14.2 ml of titrant. The calculated amounts of KNH_2 required for 1, 2, and 3 equiv are 5.0, 10.0, and 15.0, respectively, in fair agreement with the experimental data.

Preliminary Experiments with Potassium *trans*-Bis(iminodiacetato)cobaltate(III).—In an experiment similar to that described for the tris(glycinato)cobalt(III) complex, a 0.48-g sample of $K[Co(NH(CH_2CO_2)_2)_2]$ was exposed to 50 ml of liquid ammonia at −78° for 3 hr. The resulting fawn-colored solid was separated from the pink solution by filtration and purified as described above. Infrared and analytical data for this product were consistent with those for the starting material; X-ray data for the reaction product, however, indicated it to be a mixture of *cis* and *trans* isomers. *Anal.* Found: K, 10.6; C, 26.2.

A second experiment, involving a study of potassium bis(iminodiacetato)cobaltate(III) in KNH_2–ammonia solutions, was also carried out, in which a suspension of 0.667 g of $K[Co(NH(CH_2CO_2)_2)_2]$ in 100 ml of liquid ammonia was titrated with 0.407 g of KNH_2 in 20 ml of liquid ammonia. Potentiometric measurements were made after the addition of each 0.4-ml portion of amide solution.

The initial suspension of $K[Co(NH(CH_2CO_2)_2)_2]$ was pink, but upon addition of 2–3 ml of amide, the solution turned dark green and a flocculent reddish brown precipitate began to form. Precipitation of this solid continued with the addition of more titrant until the first equivalence point was reached, at which stage the supernatant liquid was colorless. No other important color changes were observed, until, with the addition of more than 3 molar equiv of amide solution, the solid product slowly turned bluish black.

The calculated amounts of KNH_2 solution required for 1 and 2 equivalents are 5.0 and 10.0 ml, respectively. Inflections were observed in the curve drawn from the data at approximately 5.2 and 11.0 ml of titrant.

Synthesis of Potassium Bis(glycinato)amidoacetatocobaltate(III), Potassium Bis(amidoacetato)glycinatocobaltate(III), and Potassium Tris(amidoacetato)cobaltate(III).—The salts $K[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$, $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$, and $K_3[Co(NHCH_2CO_2)_3]$ were prepared by titrating suspensions of tris(glycinato)cobalt(III) (*ca.* 1–2 g) in liquid ammonia (*ca.* 30 ml) with 1.0, 2.0, and 3.0 molar equiv, respectively, of potassium amide in liquid ammonia (*ca.* 30 ml). After digestion for 3 hr, the solid products were separated by filtration, washed with two 30-ml portions of ammonia, and dried *in vacuo* for 24 hr. *Anal.* Calcd for $K[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$ (red-brown): K, 12.3; C, 22.6; N, 13.2. Found: K, 12.0; C, 22.3; N, 13.8. X-Ray diffraction data: 6.55 (1.0), 6.21 (1.0), 5.60 (0.8), 5.32 (0.8), 4.50 (0.5). μ_{eff} = 2.7 BM. *Anal.* Calcd for $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$ (brown): K, 21.9; C, 20.2; N, 11.8. Found: K, 21.9; C, 19.6; N, 12.7. X-Ray diffraction data: 10.27 (1.0), 6.78 (0.8), 4.84 (0.6), 3.37 (0.8), 2.54 (0.5). μ_{eff} = 3.1 BM. *Anal.* Calcd for $K_3[Co(NHCH_2CO_2)_3]$ (gray): K, 29.7; C, 18.2; N, 10.6. Found: K, 29.1; C, 17.6; N, 11.1. X-Ray diffraction data: 10.16 (1.0), 3.36 (0.8), 3.20 (0.6), 3.13 (0.6), 2.54 (0.5), 2.25 (0.5). μ_{eff} = 3.2 BM.

Potassium tris(amidoacetato)cobaltate(III) appears unaffected by the presence of a small excess of amide ion, but with the addition of 2–3 equiv of excess KNH_2, a color change from gray to blue was observed. A sample of this blue material, prepared by the reaction of $[Co(NH_2CH_2CO_2)_3]$ with 6 equiv of KNH_2, was found to have an X-ray diffraction pattern identical with that of $K_3[Co(NHCH_2CO_2)_3]$. Analytical data for this same material, however, showed it to contain more potassium and less carbon than would be expected for the formula $K_3[Co(NHCH_2CO_2)_3]$. *Anal.* Found: K, 40.2: C, 12.0.

Synthesis of Potassium Amidodiacetato(iminodiacetato)cobaltate(III) and Potassium Bis(amidodiacetato)cobaltate(III).—The salts $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ and $K_3[Co(N(CH_2CO_2)_2)_2]$ were prepared by titrating suspensions of potassium bis(iminodiacetato)cobaltate(III) (*ca.* 1–2 g) in liquid ammonia (*ca.* 30 ml) with 1.0 and 2.0 molar equiv, respectively, of potassium amide in liquid ammonia. The solid products were separated and purified by a method exactly analogous to those described above for the synthesis of the deprotonated derivatives of $[Co(NH_2CH_2CO_2)_3]$. *Anal.* Calcd for $K_2[Co(N(CH_2CO_2)_2(NH(CH_2CO_2)_2)]$ (red-brown): K, 19.6; C, 24.1; N, 7.03. Found: K, 19.7; C, 24.2; N, 7.70. X-Ray diffraction data: 9.82 (0.5), 7.72 (0.4), 5.98 (0.4), 3.26 (1.0). μ_{eff} = 2.4 BM. *Anal.* Calcd. for $K_3[Co(N(CH_2CO_2)_2)_2]$ (red-brown): K, 26.9; C, 22.0. Found: K, 27.5; C, 21.6. X-Ray diffraction data: 9.71 (0.6), 3.79 (0.6), 3.34 (0.8), 3.30 (1.0), 2.28 (0.4), 2.09 (0.4), 2.06 (0.4). μ_{eff} = 2.7 BM.

Treatment of $K[Co(NH(CH_2CO_2)_2)_2]$ with 4 equiv of KNH_2 gave a blue, ammonia-insoluble product. Although X-ray data indicated that this material contained $K_3[Co(N(CH_2CO_2)_2)_2]$, analytical data clearly showed that this was not the only product. *Anal.* Found: K, 38.4; C, 18.4.

Properties and Reactions of $K[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$, $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$, and $K_3[Co(NHCH_2CO_2)_3]$.—All three potassium salts appear stable in a dry He atmosphere, but in air they absorb moisture and, in the case of $K_2[Co(NH_2CH_2CO_2)(NHCH_2CO_2)_2]$ and $K_3[Co(NHCH_2CO_2)_3]$, the sample turns black. All three salts are insoluble in freshly distilled THF but dissolve in water to give deep red basic solutions.

To establish that $[Co(NH_2CH_2CO_2)_3]$ may be regenerated from these deprotonated complexes, a sample of $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$ was exposed to water and the resulting solid product characterized. A 0.5-g sample of $K_2[Co(NHCH_2$-

$CO_2)_2(NH_2CH_2CO_2)]$ was dissolved in 50 ml of water and the solution was evaporated to dryness on a steam bath. The remaining reddish brown solid was washed with warm ethanol (to remove any KOH) and dried *in vacuo* over KOH pellets. The X-ray diffraction pattern for this material was identical with that for $[Co(NH_2CH_2CO_2)_3]$. *Anal.* Found: Co, 20.8.

A study was also made of the behavior of $K_3[Co(NHCH_2CO_2)_3]$ toward different methylating agents. In a typical experiment, 25 ml of freshly distilled methyl iodide was added to a 0.5-g sample of $K_3[Co(NHCH_2CO_2)_3]$ by distillation under reduced pressure, and the mixture was stirred for 10 days at 25°. After removal of excess CH_3I by filtration, the remaining brown solid was washed with liquid ammonia (to remove KI shown by X-ray data to be present in this product) and dried *in vacuo* overnight. Analytical data did not correspond to any reasonably anticipated product.

In an experiment exactly analogous to that described above, $K_3[Co(NHCH_2CO_2)_3]$ was also treated with excess methyl chloride. The reaction mixture was stirred for 2 days at $-78°$ and the gray product was separated by filtration and dried *in vacuo* for 12 hr. Infrared spectral and X-ray diffraction data for this product were identical with those for the starting material, $K_3[Co(NHCH_2CO_2)_3]$.

Properties and Reactions of $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ and $K_3[Co(N(CH_2CO_2)_2)_2]$.—Both $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ and $K_3[Co(N(CH_2CO_2)_2)_2]$ appear stable in a dry He atmosphere, but in air they absorb moisture and turn black. Both dissolve in water to give deep red basic solutions.

The salt $K[Co(NH(CH_2CO_2)_2)_2]$ may be regenerated from either of its deprotonated derivatives by treating a sample with water and isolating the resulting product. In a typical experiment, 0.5 g of $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ was dissolved in 50 ml of water and the solution was evaporated to dryness on a steam bath. The remaining brown solid was washed with warm alcohol and dried *in vacuo* over KOH pellets. The X-ray diffraction pattern for this material was identical with that for $K[Co(NH(CH_2CO_2)_2)_2]\cdot 2H_2O$. *Anal.* Calcd for $K[Co(NH(CH_2CO_2)_2)_2]\cdot 2H_2O$: K, 9.87; C, 24.3. Found: K, 10.2; C, 22.9.

Methylation of these deprotonated complexes was also attempted. Thus, 0.5 g of $K_3[Co(N(CH_2CO_2)_2)_2]$ was treated with freshly distilled methyl iodide and the mixture was stirred for 7 days at 25°. The yellowish brown solid product was separated from the pale yellow solution by filtration and dried *in vacuo* for 24 hr. Infrared spectral and X-ray diffraction data for this product were identical with those of the starting material, $K_3[Co(N(CH_2CO_2)_2)_2]$. *Anal.* Found: K, 27.7; C, 20.8.

Discussion

The data above show that protons bonded to the nitrogen atoms in $[Co(NH_2CH_2CO_2)_3]$ and $[Co(NH(CH_2CO_2)_2)_2]^-$ are sufficiently acidic to permit their removal by reaction with amide ion in liquid ammonia at $-33.5°$, *i.e.*

$$[Co(NH_2CH_2CO_2)_3] + NH_2^- \longrightarrow [Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]^- + NH_3 \quad (1)$$

$$[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]^- + NH_2^- \longrightarrow [Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]^{2-} + NH_3 \quad (2)$$

$$[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]^{2-} + NH_2^- \longrightarrow [Co(NHCH_2CO_2)_3]^{3-} + NH_3 \quad (3)$$

$$[Co(NH(CH_2CO_2)_2)_2]^- + NH_2^- \longrightarrow [Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]^{2-} + NH_3 \quad (4)$$

$$[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]^{2-} + NH_2^- \longrightarrow [Co(N(CH_2CO_2)_2)_2]^{3-} + NH_3 \quad (5)$$

Both reaction schemes have been confirmed by potentiometric titrations and by the isolation and characterization of all five reaction products as their potassium salts. The reaction products $K_3[Co(NHCH_2CO_2)_3]$ and $K_3[Co(N(CH_2CO_2)_2)_2]$ both appear to be unstable in the presence of excess amide ion. In the case of $K_3[Co(NHCH_2CO_2)_3]$ there is the possibility of further deprotonation of the glycine ligands, but this appears unlikely in view of the considerable energy necessary to achieve proton abstraction from an already negatively charged amido group.[15] A more likely explanation is that the complexes undergo partial decomposition.

It has been demonstrated that both series of deprotonated species can be reconverted to the parent complexes by treatment with water and that $K_3[Co(NHCH_2CO_2)_3]$ combines with methyl iodide to give a methylated derivative.

Since all of the products of reactions 1–5 have been isolated as solid derivatives, it was of interest to investigate the effect of successive proton abstraction from the coordinated amino and imino groups in tris(glycinato)cobalt(III) and potassium bis(iminodiacetato)cobaltate(III) upon the bonding in these materials. This can best be achieved through a general understanding of the structure of these complexes and by a comparative study of their magnetic and infrared spectral properties with those of their deprotonated derivatives.

Only preliminary X-ray structure data[16] are available for the violet *trans*-tris(glycinato)cobalt(III) complex, but studies of its absorption spectra[17–19] have shown this isomer to have the *trans,cis* or 1,2,6 configuration, with each cobalt(III) ion in an octahedral environment involving coordination to three bidentate glycine ligands. Similar studies of the absorption[14] and pmr[20] spectra of *trans*-potassium bis(iminodiacetato)cobaltate(III) have confirmed a *trans* (facial) configuration with each cobalt(III) ion coordinated to two tridentate iminodiacetate ligands.

Throughout this work only one geometric isomer of $[Co(NH_2CH_2CO_2)_3]$ and of $K[Co(NH(CH_2CO_2)_2)_2]$ was used—the one of greatest thermodynamic stability—in an attempt to simplify the interpretation of the physical data for these complexes and their deprotonated derivatives.

Most octahedrally coordinated complexes of cobalt(III) are diamagnetic,[21] and in this respect tris(glycinato)cobalt(III) and potassium bis(iminodiacetato)cobalt(III) are no exceptions. All of the deprotonated derivatives of these complexes that have been isolated in this work do, however, exhibit paramagnetism; magnetic moments in the range 2.4–3.2 BM have been observed.

A similar paramagnetic octahedral rhodium(III) complex has been reported[22] to be formed by titrating

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tris(ethylenediamine)rhodium(III) iodide with 5 equiv of KNH_2–liquid ammonia solution, but no satisfactory explanation of this observed moment was given.

The magnetic moments observed in this work are considerably less than would be normally expected for a spin-free cobalt(III) ion,[23] and it is unlikely that this is the origin of these moments, since deprotonation of the coordinated glycine and iminodiacetate ligands would be expected to increase, rather than decrease, their field strength. The presence of other deprotonated complexes containing discrete cobalt(II) or cobalt(I) species is also discounted by infrared evidence. For example, the possibility that $K_3[Co(NHCH_2CO_2)_3]$ should contain complexes having similar analytical formulations, such as $K_3[Co^{II}(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$ or $K_3[Co^{I}(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$, in any appreciable concentration is precluded by the absence of NH_2 bands in the vibrational spectra of this material (see Table I).

It is more likely that the anomalous paramagnetism is the result of π ligand-to-metal electron transfer, originating from the deprotonated amido ligands. In both the cobalt–amidoacetate and cobalt–amidodiacetate complexes, the electron pair remaining on the nitrogen atom of the deprotonated ligands would be available, and favorably orientated, for bonding with the 3d or 4p orbitals of the cobalt. Bonding of this type would help to reduce the charge density on the coordinated nitrogen atom of the amidoacetate and amidodiacetate ligands, and some evidence for a strengthening of the Co–N bond upon successive deprotonation of the $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$ complexes is provided by the infrared studies discussed below.

The effect of π-electron donation by the amidoacetate and amidodiacetate ligands on the central cobalt ion would be to reduce its effective charge, thereby making the lower oxidation states of the metal more important. Both octahedral cobalt(II) and cobalt(I) have paramagnetic ground states ($^4T_{1g}$ and $^2E_{1g}$, and $^3A_{2g}$, respectively), but even allowing for the possible effect of spin–orbit coupling and distortion by the ligand field, the observed moments (2.4–3.2 BM) do not fall entirely within the normally accepted ranges of any one of these states and it is evident that the electronic distribution about the cobalt, in both series of deprotonated complexes, can be satisfactorily accounted for only in terms of a complete molecular orbital description.

π-Electron donation by a coordinated amido ligand to a 3d transition metal is also important[24] in related complexes such as bis(*o*-phenylenediamido)nickel, $[Ni(C_6H_4(NH)_2)_2]$ and bis(*o*-mercaptoanilido)nickel, $[Ni(C_6H_4(NH)S)_2]$. Recently, a qualitative molecular orbital model for the bonding in these and similar complexes has been described.[25]

It was hoped that additional evidence for this type of ligand-to-metal electron transfer in the deprotonated derivatives of $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$ could be obtained from studies of their ultraviolet and visible spectra. This, unfortunately, was not possible owing to the instability of these materials in water and other protonated solvents and their insolubility in other solvents of high dielectric constant. However, the esr spectra for the same materials in the solid state were consistent with their magnetic moments, although the recorded signals were weak and in some cases rather poorly defined.

The infrared spectrum of tris(glycinato)cobalt(III) has been recorded by Quagliano,[19] and empirical assignments for some of the bands in this spectrum have been suggested by Mori, *et al.*[13] Complete assignments for the vibrational spectrum of potassium bis(iminodiacetato)cobaltate(III) have not been made.

In the absence of theoretical calculations, our assignments for the vibrational spectra of $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$ have been made either from studies of the infrared spectra of their deuterated analogs or by comparison with the assignments for similar compounds. Assignments for the deprotonated derivatives have been made by comparison with the parent compounds.

CO_2 Vibrations.—Bands due to the vibrations of the carboxylate group have been identified with reference to earlier studies of the spectra of glycine[19,26,27] and iminodiacetic acid[28] complexes. Although these bands are not significantly affected by deuteration, they are all shifted to some extent by deprotonation. This is particularly true of the carboxylate stretching modes. In both the $[Co(NH_2CH_2CO_2)_3]$ and the $K[Co(NH(CH_2CO_2)_2)_2]$ series, successive deprotonation of the coordinated amino and imino groups is paralleled by a successive reduction in the frequency separation of the ν_{asym}(OCO) and ν_{sym}(OCO) vibrations. A similar reduction in frequency separation has been previously observed in the spectra of the deprotonated derivatives of bis(β-alaninato)nickel(II);[9] this was attributed to a reduction in the covalent character of the metal–oxygen bonding.

An alternative explanation of these changes in $[\nu_{asym}(OCO) - \gamma_{sym}(OCO)]$ is that they are due to a reduction in the effect of hydrogen bonding in these complexes. In solid $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$, hydrogen bonding of the type $NH\cdots OC$, involving the coordinated carboxylate and amino groups, is important.[29] In the case of most of their deprotonated derivatives isolated in this work, however, this is no longer true. For example, there is no way that bonding of this type could exist in $K_3[Co(N(CH_2CO_2)_2)_2]$, and even in derivatives such as $K_3[Co(NHCH_2CO_2)_3]$, the excess electron density on

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the coordinated amido groups in this complex would drastically reduce the effect of NH···OC bonding.

NH_2 and NH Vibrations.—The fundamental vibrations of the NH_2 group have been identified in the spectra of a number of amino acid complexes,[13,19,25] and agreement appears to have been reached concerning these assignments except for the NH_2 wagging and twisting modes (for alternative assignments see work by Nakamoto,[26] Quagliano,[19] and Mori,[13] *et al.*). The assignments in Table I for these vibrational modes are consistent with our deuteration studies.

The vibrations of the imino group have been identified with reference to studies of the spectra of substituted diethylenetriamine complexes.[30]

The intensity of all the NH_2 and NH vibrations in the spectra of the tris(glycinato)cobalt(III) and potassium bis(iminodiacetato)cobaltate(III) complexes are markedly reduced upon successive deprotonation of these materials. The spectra of both $K[Co(NHCH_2CO_2)(NH_2CH_2CO_2)_2]$ and $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$ show absorptions of reduced intensity attributable to the NH_2 stretching, wagging, and twisting modes. Even these bands disappear, however, in the spectrum of the triply deprotonated complex, $K_3[Co(NHCH_2CO_2)_3]$.

Similarly, in the case of $K[Co(NH(CH_2CO_2)_2)_2]$ and its derivatives, the NH stretching and bending motions, which appear as weak bands in $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ are absent from the spectrum of $K_3[Co(N(CH_2CO_2)_2)_2]$.

It is interesting to note the appearance of a new band at 1450 cm^{-1} in the spectra of $K_2[Co(NHCH_2CO_2)_2(NH_2CH_2CO_2)]$ and $K_3[Co(NHCH_2CO_2)_3]$ which is not present in the starting material. This band has been assigned to the NH bending mode, and its presence in the spectra of these complexes may be cited as additional evidence that deprotonation of the glycine ligands in $[Co(NH_2CH_2CO_2)_3]$ involves the removal of only one proton from each coordinated amino group.

The regions of absorption of the CH_2 vibrational modes have been well established[31] as have those due to the skeletal C–N and C–C vibrations;[26,28,32] since only the CH_2 rocking mode is significantly affected by deprotonation (owing to coupling with the analogous NH_2 vibration), detailed discussion of these bands is not necessary.

Co–N and Co–O Vibrations.—Previous assignments of the "far"-infrared spectra of $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$ have not been made. Shimanouchi and Nakagawa[33] have assigned the Co–N stretching mode at 503 cm^{-1} for $[Co(NH_3)_6]Cl_3$ and Powell and Sheppard[34] have attributed the same vibration in $[Co(en)_3]^{3+}$ to a band at 583 cm^{-1}. Both $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$ exhibit a number of bands in the 500–600-cm^{-1} region (see Table I), and it is not possible, on an empirical basis, to discern which of these are due to the ν(Co–N) vibration. Some are most probably ring deformation modes.

Shimanouchi and Nakagawa[33] have also identified a band at 325 cm^{-1} in the spectrum of $[Co(NH_3)_6]Cl_3$ with the N–Co–N bending mode, and it appears likely that similar bands at *ca.* 350 cm^{-1} in $[Co(NH_2CH_2CO_2)_3]$ and $K[Co(NH(CH_2CO_2)_2)_2]$ are due to this mode.

Although it was not possible to record the ultraviolet spectra of the deprotonated derivatives of tris(glycinato)cobalt(III) and potassium bis(iminodiacetato)cobaltate(III), additional evidence of ligand-to-metal electron transfer in these materials should be provided by studies of their infrared spectra and, in particular, by studies of the vibrations of the Co–N bonds.

In view of the uncertainty in assigning the ν(Co–N) vibration in $[Co(NH_2CH_2CO_2)_3]$ and its derivatives, it is doubtful whether any definite conclusions can be drawn concerning the effect of deprotonation on this vibration. It would appear, however, that none of the bands between 500 and 600 cm^{-1} in the spectrum of $[Co(NH_2CH_2CO_2)_3]$ is significantly shifted in the spectrum either of $K_2[Co(NH_2CH_2CO_2)(NHCH_2CO_2)_2]$ or of the other derivatives.

The evidence is, however, more satisfactory in the case of $K[Co(NH(CH_2CO_2)_2)_2]$ and its derivatives. Here, the strongest member of the triplet between 538 and 571 cm^{-1} in the spectrum of the parent material (at 538 cm^{-1}) appears at 561 and 560 cm^{-1}, respectively, in the spectra of $K_2[Co(N(CH_2CO_2)_2)(NH(CH_2CO_2)_2)]$ and $K_3[Co(N(CH_2CO_2)_2)_2]$. Similar shifts of *ca.* 20 cm^{-1} are observed in the absorptions due to the N–Co–N bending mode. Both the ν(Co–N) and δ(Co–N) band shifts are consistent with an increase in metal–nitrogen bond strength and are indicative of a transfer, in the direction of the metal, of charge remaining on the coordinated amino nitrogen after removal of a proton.

The Co–O stretching mode appears in the spectra of both parent materials as a strong absorption centered at *ca.* 450 cm^{-1}. Besides some reduction in intensity, neither set of bands is significantly affected by deprotonation. This being so, the previously discussed shifts in the carboxylate stretching modes are probably the result of changes in intermolecular hydrogen bonding.

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