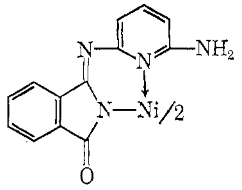
the latter arrangement, it should be possible to remove the uncomplexed iminoisoindoline ring by hydrolysis, whereas, in the former, this should be excluded because both rings are coordinated to the nickel ion. Such is found to be the case. Hydrolysis with a 50% hydrochloric acid solution gives 2 moles of phthalic acid/mole of starting complex. The average per cent error for four hydrolyses runs was 11% based on theoretical recovery of phthalic acid. The resulting complex, bis[1-(2-aminopyrid-6-yl)-1-imino-3-oxoisoindolinato]nickel(II), abbreviated $Ni(DIPN)_2$, was isolated and characterized by elemental analyses, magnetic susceptibility measurements, molar conductance, and visible spectroscopy. The structure is depicted in VII. Because of the onset of a very strong charge-transfer band at very low energies, no assignment of d–d transitions could be made. Final corroboration for the structure is found in the infrared spectrum where the NH_2 stretching vibrations (although quite weak) occur at 3350 and 3450 cm^{-1}.



VII

On the basis of the previously described reactions, and minimizing the possibility of extensive ligand reorganization, it is concluded that the coordinating sites in $[Ni(DIP)Cl_2]$ are the pyridine nitrogen and one of the isoindoline ring nitrogen atoms.

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Deprotonation of Glycine and β-Alanine Complexes of Nickel(II)

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Treatment of bis(glycinato)nickel(II) and bis(β-alaninato)nickel(II) with potassium amide in liquid ammonia at −33.5° has led to the isolation and characterization of the compounds $KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$, $K_2Ni(NHCH_2CO_2)_2$, $KNi(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)$, and $K_2Ni(NHCH_2CH_2CO_2)_2$. Both cases correspond to the successive removal of protons from the ligand nitrogen atoms; the doubly deprotonated species represent the maximum number of protons that may be abstracted under these conditions. The infrared spectra of these and the parent complexes have been studied to examine the effect of proton abstraction upon the nature of the metal–ligand bonds.

Earlier work has established that protons associated with the ligand nitrogen atoms in ethylenediamine[1–8] and diethylenetriamine[9,10] complexes are sufficiently acidic to permit their successive removal in appreciably basic media. An extension of these studies has since shown that proton abstraction from a coordinated amino group can be achieved with a number of other bidentate ligands. Here we report results from studies of the deprotonation of glycine and β-alanine complexes of nickel(II); this work was of particular interest since evidence for the successful deprotonation of the amino group coordinated to a 3d series transition metal has not been demonstrated previously.

Experimental Section

Methods.—Reactions in liquid ammonia and procedures for handling the products thereof were the same as described elsewhere.[11] The 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.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kv and 15 ma. Exposure times were 12–18 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.

Nickel was determined gravimetrically as the dimethylglyoximate.[12] 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.

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TABLE I

INFRARED SPECTRA IN THE 200–3800-CM^{-1} REGION

$Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$	$KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$	$K_2Ni(NHCH_2CO_2)_2$	$Ni(NH_2CH_2CH_2CO_2)_2 \cdot 2H_2O$	$KNi(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)$	$K_2Ni(NHCH_2CH_2CO_2)_2$	Tentative assignments
3430 s			3430 s			ν(OH)
3330 s	3340 s	3340 s	3330 s	3335 s	3340 s	
3275 s	3185 s	3185 s	3280 s	3260 s	3265 s	ν(NH), $\nu(NH_2)$
3205 s			3210 m, sh	3175 m	3180 m	
2985 w	2940 m	2955 w	2990 w	2980 s	2950 s	$\nu_a(CH_2)$
			2965 w			
			2940 w			
2940 w			2895 w	2890 m	2880 m	$\nu_s(CH_2)$
1612 vs						$\delta(NH_2)$
1593 vs	1585 vs	1584 vs	1598 vs	1575 vs	1570 vs	$\nu_a(CO_2)$
1440 s	1425 s	1425 s	1463 m	1485 m	1485 m	$\delta(CH_2)$
1414 s	1400 vs	1395 vs	1418 s	1435 s	1430 s	$\nu_s(CO_2)$
			1386 s		1390 s	
1350 m	1340 m	1345 m	1326 m	1315 m	1315 m	$\omega(CH_2)$
1307 m	1321 w	1321 m				
1287 w	1255 vw	1260 w	1267 m	1267 w		
				1234 m	1235 m	
1188 vw	1217 w	1218 m	1171 w	1164 w	1165 w	$\delta(CH_2)$
1101 s	1104 w		1127 m			$\delta(NH_2)$
1101 s	1114 w	1135 w	1082 m	1095 w	1096 w	ν(CN)
1043 m	1039 m	1040 m	978 m	971 m		$\omega(NH_2)$
				1041 m	1043 m	
950 w	944 w	945 vw	1009 w	1003 w	1009 w	ν(CC)
				930 m	930 m	
				921 m	922 m, sh	
916 w	903 w, sh	904 w	897 m	890 m	892 m	$\rho(CH_2)$
	893 m	895 w				
	854 m	857 w	875 m	867 w, sh	857 w, sh	
				797 m	798 m	
741 m	724 m	726 m	725 m	708 m	709 m	$\delta(CO_2)$
677 m	667 m	673 m				
		664 m				
630 m			655 m	660 m		$\rho(NH_2)$
597 m	597 w	593 w	625 m	616 m	601 m	$\rho(CO_2)$
520 m	510 w	508 w	510 m	486 m	483 m	
			433 m	407 m	405 m	
435 vw	486 vw	482 vw, sh	366 m	380 m	380 m	ν(NiN)
335 m			337 m	346 m	355 m	
			307 m			
287 m	285 m		285 m(?)			ν(NiO)

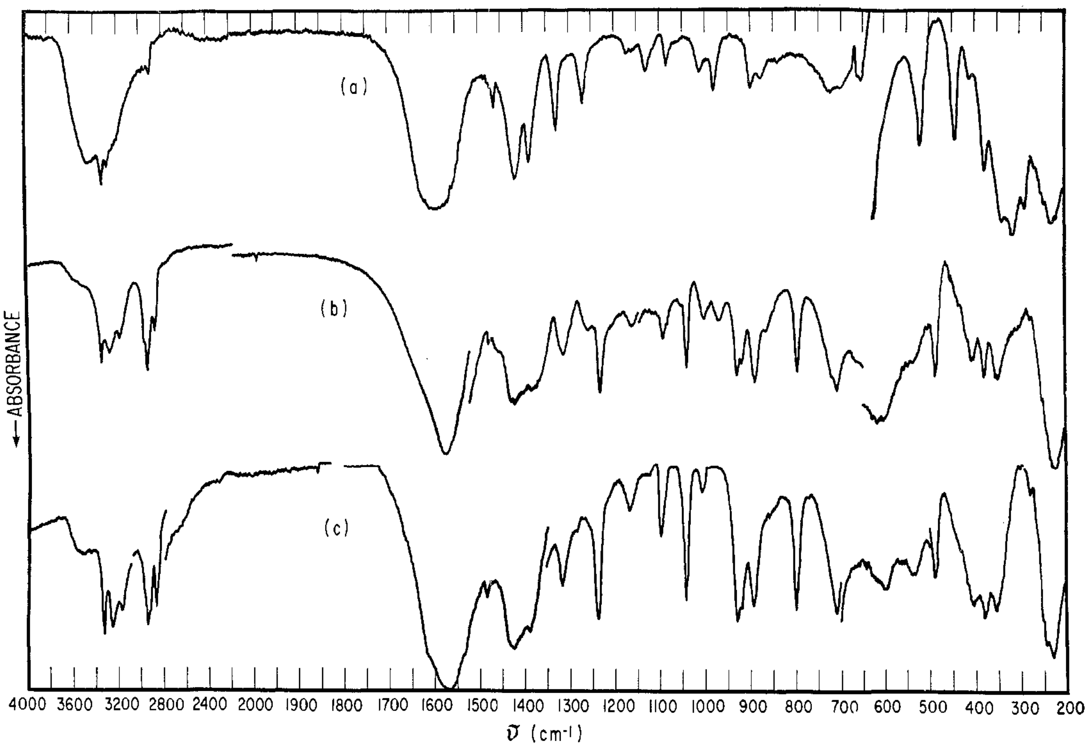

Figure 1.—The infrared spectra of (a) $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$, (b) $KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$, and (c) $K_2Ni(NHCH_2CO_2)_2$.

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

Bis(glycinato)nickel(II) dihydrate, $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$, was prepared by the method of Stosick.[13] *Anal.* Calcd for $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$: Ni, 24.2; C, 19.8. Found: Ni, 24.2; C, 19.9. X-Ray diffraction data (*d* spacings (A), relative in-

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[13] A. J. Stosick, *J. Am. Chem. Soc.*, **67**, 365 (1945).

tensities in parentheses): 6.80 (1.0), 5.23 (0.9), 4.73 (1.0), 3.70 (0.7), 3.29 (0.7), 2.63 (0.7).

Bis(β-alaninato)nickel(II) dihydrate, $Ni(NH_2CH_2CH_2CO_2)_2\cdot 2H_2O$, was prepared as described by Nakamoto, *et al.*[14] *Anal.* Calcd for $Ni(NH_2CH_2CH_2CO_2)_2\cdot 2H_2O$: Ni, 21.7; C, 26.6. Found: Ni, 21.5; C, 26.6. X-Ray diffraction data: 8.07 (1.0), 5.69 (0.9), 4.74 (0.9), 4.36 (0.7), 3.42 (0.7).

Bis(α-methylalaninato)nickel(II) dihydrate, $Ni[NH_2C(CH_3)_2CO_2]_2\cdot 2H_2O$, was prepared as described for the bis(glycinato)nickel(II) complex. *Anal.* Calcd for $Ni[NH_2C(CH_3)_2CO_2]_2\cdot 2H_2O$: Ni, 19.6; C, 32.2. Found: Ni, 19.2; C, 32.2. X-Ray diffraction data: 10.39 (1.0), 5.24 (0.8), 5.06 (0.6), 4.10 (0.5), 3.04 (0.6).

All three dihydrates were converted to the anhydrous materials by heating at *ca.* 150° for 2 hr and allowing the products to cool *in vacuo* over KOH pellets. The composition of the dehydrated complexes was established by analysis and by infrared spectroscopy.[15] *Anal.* Calcd for $Ni(NH_2CH_2CO_2)_2$: Ni, 28.4; C, 23.2. Found: Ni, 28.4; C, 23.2. X-Ray diffraction data: 7.56 (1.0), 6.41 (0.6), 4.25 (0.4), 3.19 (0.4), 3.05 (0.3), 2.80 (0.3), 2.27 (0.3). Calcd for $Ni(NH_2CH_2CH_2CO_2)_2$: Ni, 25.0; C, 30.7. Found: Ni, 24.7; C, 30.5. X-Ray diffraction data: 8.46 (1.0), 6.91 (0.2), 4.86 (0.2), 3.46 (0.3), 3.14 (0.7), 2.22 (0.5). Calcd for $Ni[NH_2C(CH_3)_2CO_2]_2$: C, 36.6. Found: C, 36.5. X-Ray diffraction data: 9.98 (1.0), 8.34 (0.9), 6.19 (0.3), 5.57 (0.4), 4.57 (0.6), 4.17 (0.3), 4.04 (0.3).

Preliminary Experiments.—Preliminary experiments were carried out in order to establish whether or not $Ni(NH_2CH_2CO_2)_2$ and $Ni(NH_2CH_2CH_2CO_2)_2$ are solvated, solvolyzed, or ligand-substituted by ammonia.

A 0.8-g sample of $Ni(NH_2CH_2CO_2)_2$ was treated with 20 ml of liquid ammonia for 3 hr at −78°. The resulting deep blue precipitate 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. *Anal.* Calcd for $Ni(NH_2CH_2CO_2)_2\cdot 2NH_3$: Ni, 24.4; C, 20.0. Found: Ni, 24.4; C, 20.1. X-Ray diffraction data: 7.69 (0.8), 6.43 (0.4), 3.21 (0.6), 1.95 (1.0), 1.68 (0.3). Similar treatment of $Ni(NH_2CH_2CH_2CO_2)_2$ with liquid ammonia yielded the blue bis(β-alaninato)nickel(II) diammoniate. *Anal.* Calcd for $Ni(NH_2CH_2CH_2CO_2)_2\cdot 2NH_3$: Ni, 21.8; C, 26.8. Found: Ni, 21.9; C, 26.7. X-Ray diffraction data: 8.18 (1.0), 5.71 (0.3), 4.75 (0.3), 3.25 (0.4), 1.99 (0.8).

Synthesis of Potassium Amidoacetato(glycinato)nickelate(II).—To a suspension of 2.94 g of $Ni(NH_2CH_2CO_2)_2$ in *ca.* 30 ml of ammonia at −33.5° was added slowly a solution containing 1.01 molar equiv of KNH_2 in 20 ml of ammonia. After a digestion period of 3 hr, the resulting orange precipitate was separated from the colorless solution by filtration and washed with two 30-ml portions of ammonia. All remaining solvent was removed under reduced pressure and the solid reddish brown residue was transferred to the drybox for removal of samples. *Anal.* Calcd for $KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$: Ni, 24.0; C, 19.6; N, 11.4. Found: Ni, 24.0; C, 18.9; N, 11.3. X-Ray diffraction data: 10.10 (1.0), 3.37 (0.9), 3.21 (0.6), 3.12 (0.6), 2.53 (0.4), 2.24 (0.3).

Properties and Reactions of Potassium Amidoacetato(glycinato)nickel(II).—The salt, $KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$, appears to be stable in a dry He atmosphere, but in air it rapidly absorbs moisture and turns green. An X-ray diffraction pattern of this green decomposition product showed lines attributable to bis(glycinato)nickel(II) dihydrate, $Ni(NH_2CH_2CO_2)\cdot 2H_2O$. The potassium salt dissolves readily in water to give a blue basic solution.

To establish further that bis(glycinato)nickel(II) may be regenerated from the deprotonated complex, a sample was exposed to water and the resulting solid product characterized. A 0.5-g sample of $KNi(NH_2CH_2CO_2)(NH_2CH_2CO_2)$ was dissolved in 20 ml of water and the solution concentrated on a steam bath. On cooling, a blue crystalline precipitate was obtained. This was separated by filtration, washed with alcohol and ether, and dried *in vacuo* over KOH. The infrared data showed that this product was identical with $Ni(NH_2CH_2CO_2)_2\cdot 2H_2O$. *Anal.* Calcd for $Ni(NH_2CH_2CO_2)_2\cdot 2H_2O$: C, 19.8. Found: C, 19.7.

Synthesis of Potassium β-Amidopropionato(β-alaninato)nickelate(II).—This reaction was carried out with 2.16 g of $Ni(NH_2CH_2CH_2CO_2)_2$ (0.92 mmole) in *ca.* 30 ml of liquid ammonia by titrating dropwise with 16 ml of 0.575 *M* KNH_2 (0.92 mmole). After a digestion period of 3 hr, the colorless supernatant solution was transferred to a trap and the orange, insoluble product was washed with two 30-ml portions of ammonia and dried *in vacuo* for 24 hr. The solid reddish product was transferred to the drybox for removal of samples. *Anal.* Calcd for $KNi(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)$: Ni, 21.5; C, 26.4; N, 10.3. Found: Ni, 22.0; C, 25.6; N, 10.6. X-Ray diffraction data: 12.01 (0.8), 4.21 (0.4), 3.54 (0.4), 3.23 (1.0), 3.04 (0.4), 2.00 (0.5).

Synthesis of Potassium Bis(amidoacetato)nickelate(II).—To a suspension of 1.10 g of $Ni(NH_2CH_2CO_2)_2$ in *ca.* 50 ml of ammonia was added slowly 18 ml of liquid ammonia containing KNH_2 prepared from 0.432 g of K (2.08 molar equiv). After a digestion period of 3 hr, the orange product was separated from the colorless solution by filtration and purified by a method exactly analogous to that used in the synthesis of the potassium amidoacetato(glycinato)nickel(II) complex. The final product was reddish brown but lighter than the singly deprotonated material. *Anal.* Calcd for $K_2Ni(NHCH_2CO_2)_2$: Ni, 20.7; C, 17.0; N, 9.90. Found: Ni, 21.1; C, 16.5; N, 9.70. X-Ray diffraction data: 10.21 (1.0), 5.73 (0.5), 5.45 (0.6), 3.37 (0.8), 2.53 (0.5), 2.00 (0.7).

The same product (identified by infrared and X-ray data) was obtained by treating $Ni(NH_2CH_2CO_2)_2$ with 3 molar equiv of KNH_2. *Anal.* Found: C, 16.5; N, 9.79.

Synthesis of Potassium Bis(β-amidopropionato)nickelate(II).—To a suspension of 1.37 g of $Ni(NH_2CH_2CH_2CO_2)_2$ in *ca.* 50 ml of ammonia at −33.5° was added slowly a solution containing 2.07 molar equiv of KNH_2 in 20 ml of ammonia. After a digestion period of 3 hr, the orange product was separated from the reddish solution by filtration and purified as described above. The residue was reddish brown but lighter in color than the singly deprotonated material. *Anal.* Calcd for $K_2Ni(NHCH_2CH_2CO_2)_2$: Ni, 18.9; C, 23.2; N, 9.00. Found: Ni, 18.6; C, 23.2; N, 8.67. X-Ray diffraction data: 12.18 (1.0), 4.21 (0.4), 3.56 (0.4), 3.22 (0.9), 3.05 (0.4), 2.10 (0.5).

The same deprotonation was effected upon treatment of $Ni(NH_2CH_2CH_2CO_2)_2$ with 4 molar equiv of KNH_2. *Anal.* Found: C, 23.0; N, 8.73.

Synthesis of Potassium α-Amidoisobutyrato(α-methylalaninato)nickelate(II).—A 1.05-g sample of $Ni[NH_2C(CH_3)_2CO_2]_2$ was suspended in 50 ml of ammonia at −33.5° and treated slowly with a solution containing 1.0 molar equiv of KNH_2 in 20 ml of ammonia. After digestion for 1 hr, the orange precipitate was separated from the colorless solution by filtration and purified as described above. *Anal.* Calcd for $KNi[NHC(CH_3)_2CO_2][NH_2C(CH_3)_2CO_2]$: C, 31.9; N, 9.30. Found: C, 30.9; N, 9.95. This product is extremely unstable and decomposes rapidly in the presence of only minute traces of water. An X-ray diffraction pattern was obtainable only with short exposure times; only the following three *d* spacings (A) could be detected with certainty (relative intensities in parentheses): 10.84 (1.0), 5.32 (0.6), 3.60 (0.1). An infrared spectrum was obtained (see Discussion), but the results are not given in detail here.

Efforts to effect further deprotonation, *i.e.*, to synthesize potassium bis(α-amidoisobutyrato)nickelate(II) by treatment of $Ni[NH_2C(CH_3)_2CO_2]_2$ with 2 molar equiv of KNH_2 in ammonia, failed to provide identifiable products.

Discussion

The data presented above show that the amino groups in $Ni(NH_2CH_2CO_2)_2$ and $Ni(NH_2CH_2CH_2CO_2)_2$

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(15) J. Fujita, K. Nakamoto, and M. Kobayashi, *ibid.*, **78**, 3963 (1956).

are sufficiently acidic to permit the abstraction of a maximum of one proton from each ligand nitrogen by reaction with the basic amide ion in liquid ammonia at −33.5°, *i.e.*

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

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

Similarly

$$Ni(NH_2CH_2CH_2CO_2)_2 + NH_2^- \longrightarrow [Ni(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)]^- + NH_3 \quad (3$$

$$[Ni(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)]^- + NH_2^- \longrightarrow [Ni(NHCH_2CH_2CO_2)_2]^{2-} + NH_3 \quad (4)$$

The products of reactions 1–4 have been isolated as the potassium salts and characterized; it has been demonstrated that these species can be reconverted to the parent complex by treatment with water. That reactions 2 and 4 represent the maximum extent of reaction at −33.5° was demonstrated by the fact that both $[Ni(NHCH_2CO_2)_2]^{2-}$ and $[Ni(NHCH_2CH_2CO_2)_2]^{2-}$ are unreactive toward excess amide ion over several hours. This, however, does not preclude the possibility of more extensive deprotonation at higher temperatures. In particular, there is the possibility of further deprotonation of the ligand nitrogen atoms although recent work on the behavior of bipyridyl(ethylenediamine)platinum(II) iodide toward excess potassium amide has shown[16] that the removal of a second proton from the same amino group cannot be achieved even at 25°.

Moreover, for the reactions proposed in (1)–(4), it is assumed that the reactions of bis(glycinato)nickel(II) and bis(β-alaninato)nickel(II) with amide ion proceed exclusively by proton abstraction from the coordinated amino groups. An alternative path could involve deprotonation of the α-methylene groups. Recent nmr studies[17] of $[Co(en)_2(NH_2CH_2CO_2)](NO_3)_2$ and of the corresponding α-alanine complex have shown that the α-methylene hydrogen atoms in the coordinated amino acids are labile. This behavior is consistent with an earlier reported observation[18] that bis(glycinato)copper(II) reacts with aldehydes and ketones to form β-hydroxyamino acids.

Nevertheless, it is unlikely that the α-methylene groups are involved in the deprotonation of these nickel(II)–amino acid complexes. In the first place, both solid products isolated from reactions 1 and 2 show strong peaks in their infrared spectra which could only be attributed to CH_2 vibrations. Furthermore, it is possible to deprotonate the nickel(II) complex of an aminocarboxylic acid in which the α carbon atom of the chelated ligand is not directly bonded to hydrogen. Thus, treatment of bis(α-methylalaninato)nickel(II) with amide ion at −33.5° was found to yield potassium α-amidoisobutyrato(α-methylalaninato)nickelate(II), a solid product analogous to those obtained from reactions 1 and 3.

$$Ni[NH_2C(CH_3)_2CO_2]_2 + NH_2^- \longrightarrow Ni[NHC(CH_3)_2CO_2][NH_2C(CH_3)_2CO_2]^- + NH_3 \quad (5)$$

X-Ray structure analysis[13] has established that the two glycinato ions in $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$ coordinate to the metal in a *trans*-square-planar structure. A similar spatial arrangement of the β-alaninato ions has been shown[19] to exist in $Ni(NH_2CH_2CH_2CO_2)_2 \cdot 2H_2O$.

The infrared spectrum of $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$ has been reported[20] and empirical assignments for these bands have been suggested.[14,21–24] Condrate and Nakamoto[25] have carried out a normal coordinate analysis on the bis(glycinato)nickel(II) dihydrate complex using a 1:1 (metal:ligand) approximation. Our assignments for $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$ are consistent with those proposed by Nakamoto; the assignments for the deprotonated complexes, $KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$ and $K_2Ni(NHCH_2CO_2)_2$, were made by comparison with the parent compound.

Complete assignment for the vibrational spectra of bis(β-alaninato)nickel(II) dihydrate has not been made. Nakamoto, *et al.*,[14] have assigned the bands at 1607 and 1413 cm^{-1} to carboxylate stretching modes. Sharma, Mathur, and Biswas[26] have assigned the bands at 3333, 3291, and 3181 cm^{-1} to N–H stretching vibrations and suggest that the reduction in frequency of these bands compared with those for β-alanine can be taken as evidence of the covalent nature of the Ni–N bond. In this work, tentative assignments for the spectrum of $Ni(NH_2CH_2CH_2CO_2)_2 \cdot 2H_2O$ have been made by comparison with those for the bis(glycinato)nickel(II) dihydrate and bis(α-alaninato)nickel(II) trihydrate complexes.[27]

A comparison of the infrared spectra of the two series of deprotonated species with those of the corresponding parent compounds reveals certain important differences which are characteristic[7,10] of proton abstraction from a coordinated amino nitrogen atom. Of particular interest is the effect of deprotonation on the metal–nitrogen stretching frequency. This vibrational mode has been assigned in bis(glycinato)nickel(II) and in bis(β-alaninato)nickel(II) to the bands at 435 and 366 cm^{-1}, respectively. The same vibrations appear in the spectra of the deprotonated complexes at higher frequencies. Such shifts are indicative[7] of a transfer, in the direction of the metal, of charge remaining on the coordinated amino nitrogen after removal of a proton. In the case of the nickel–glycine derivatives these increases in the energy of the Ni–N

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vibrations are considerably larger than those observed during the successive deprotonation of either [Rh(en)$_3$]I$_3$[7] or [Pt(bipy)(en)]I$_2$.[16]

The NH$_2$ vibrational modes are also affected by deprotonation. The NH$_2$ stretching and bending vibrations either disappear in the spectra of the singly deprotonated species or are reduced in intensity. As for the doubly deprotonated complexes, KNi(NHCH$_2$CO$_2$)$_2$ and K$_2$Ni(NHCH$_2$CH$_2$CO$_2$)$_2$, since neither of these contain the amino group, no bands characteristic of NH$_2$ vibrations should be observed. Most probably, the intense bands between 3150 and 3350 cm^{-1} are due to crystal-field splitting of the N–H stretching mode. In the case of K$_2$Ni(NHCH$_2$CO$_2$)$_2$ this vibration appears as a doublet, and in the case of K$_2$Ni(NHCH$_2$CH$_2$CO$_2$)$_2$, as a triplet.

The Ni–O stretching mode in Ni(NH$_2$CH$_2$CO$_2$)$_2$ has been assigned empirically by Nakamoto[25] to a band at 280 cm^{-1}, but there is some doubt as to whether the corresponding band at 285 cm^{-1} in bis(β-alaninato)nickel(II) could also be assigned to this vibrational mode, especially since analogous bands are not observed in the spectrum of either KNi(NHCH$_2$CH$_2$CO$_2$)(NH$_2$CH$_2$CH$_3$CO$_2$) or K$_2$Ni(NHCH$_2$CH$_2$CO$_2$)$_2$. Possibly deprotonation of these complexes causes a reduction in the covalent character of the Ni–O bonds, and the ν(Ni–O) vibrations are shifted to much lower frequencies in the deprotonated complexes. A similar conclusion can be drawn from the frequency shifts of the carboxylate stretching modes.

The asymmetric and symmetric COO stretching vibrations are normally very susceptible to the effects of coordination and intermolecular interaction,[28] and Nakamoto, *et al.*,[14] have suggested that whenever there is a decrease in the covalent character of the Ni–O bonds, there is a corresponding decrease in the frequency separation of the two COO stretching modes. In the spectra of KNi(NHCH$_2$CH$_2$CO$_2$)(NH$_2$CH$_2$CH$_2$CO$_2$) and K$_2$Ni(NHCH$_2$CH$_2$CO$_2$)$_2$, the COO asymmetric stretch appears at a lower frequency, and the COO symmetric stretch at a higher frequency, than in the parent Ni(NH$_2$CH$_2$CH$_2$CO$_2$)$_2$. This is consistent with a weakening of the Ni–O bond with successive deprotonation. A similar weakening of the Ni–O bond is not unequivocably confirmed in the case of the nickel–glycine derivatives, however, where only the asymmetric COO stretching frequency shifts in the expected direction.

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[28] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 203.

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1,2-Bis-Substituted *o*-Carborane Complexes. II.[1] Nickel(II) and Cobalt(II) Complexes Derived from the Ligand 1,2-Bis(mercapto)-*o*-carborane

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Some nickel(II) and cobalt(II) salts have been found to react readily with 1,2-bis(mercapto)-*o*-carborane in the presence of stabilizing phosphorous ligands or the tetraethylammonium cation to yield square-planar MS$_2$P$_2$ and MS$_4^{2-}$ complexes. Electronic spectra of the nickel complexes are discussed.

Introduction

In a previous communication we reported the synthesis of four-coordinate nickel(II) complexes of 1,2-bis(diphenylphosphino)-*o*-carborane and B-bromo-*o*-carboranes.[1] Ligand-exchange data suggested that the order of stability of the series described was $[((C_6H_5)_2P)_2B_{10}H_{10}C_2]NiCl_2 < [((C_6H_5)_2P)_2B_{10}H_{10}C_2]_2NiCl_2 < [((C_6H_5)_2P)_2B_{10}H_9BrC_2]_2NiCl_2 < [((C_6H_5)_2P)B_{10}H_8Br_2C_2]_2NiCl_2 < [((C_6H_5)_2P)_2B_{10}H_7Br_3C_2]_2NiCl_2$. This order is probably a consequence of increased π bonding between phosphorus and nickel due to an increase in the electronegativity of the borane system with increased halogen substitution. It is also conceivable that the observed stability is a result of electron delocalization of a pseudo-aromatic nature involving the –M–P–carborane–P– cyclic system.

Gray and co-workers have reported the electronic structures of stable square-planar complexes of various transition metals with bidentate sulfur ligands capable of extensive π delocalization.[2] The recent synthesis of 1,2-bis(mercapto)-*o*-carborane provides a potential bidentate sulfur ligand comparable to both the phosphino carboranes and the sulfur ligands of Gray, *et al.* It was of interest to attempt to prepare complexes utilizing 1,2-bis(mercapto)-*o*-carborane as the chelating ligand and examine the chemical properties and electronic spectra in order to obtain information on the

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[1] For the first paper in this series see H. D. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 1817 (1965)

[2] H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 240 (1965).