CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF TENNESSEE, MARTIN, TENNESSEE, AND THE DEPARTMENT OF CHEMISTRY,
ILLINOIS INSTITUTE OF TECHNOLOGY, TECHNOLOGY CENTER, CHICAGO, ILLINOIS 60616

Infrared Spectra and Normal Coordinate Analysis of Metal Oxamido Complexes[1]

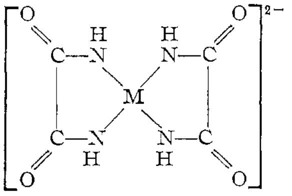
BY PETER X. ARMENDAREZ AND KAZUO NAKAMOTO

Received December 27, 1965

The infrared spectra of bis(oxamido) complexes with Cu(II), Ni(II), and Pd(II) have been measured from 4000 to 200 cm^{-1}. It has been concluded that the oxamido anion coordinates through both nitrogen atoms in these complexes. A normal coordinate analysis has been carried out on the Ni(II) complex including its deuterio and N^{15} analogs. The bands near 455 and 360 cm^{-1} have been assigned to the coupled Ni—N stretching and C=O in-plane bending vibrations, while that at 290 cm^{-1} has been assigned to a pure Ni—N stretching vibration. The Ni—N stretching force constant has been estimated to be 0.73 mdyne/A. Previous empirical band assignments have been corrected on the basis of the calculation of potential energy distribution in each normal vibration.

Introduction

Oxamide ($NH_2COCONH_2$) acts as a bidentate ligand and may coordinate to the metal ion through both nitrogen atoms, both oxygen atoms, or one nitrogen and one oxygen atom. In spite of this interesting property of oxamide, very little structural work has been carried out since Hoffmann and Ehrhardt[2] first prepared its Cu(II) and Ni(II) complexes in 1913. The infrared study of bis(oxamido) complexes of Cu(II) and Ni(II) was first carried out by Kuroda, *et al.*,[3] who concluded that the square-planar diimido structure (V_h symmetry) such as shown below gives the best agreement with the observed spectra. This structure is analogous to that of bis(biureto)copper(II) tetrahydrate (violet form), for which an X-ray structural determination[4] and an infrared study[5] have been reported.



I

However, bis(oxamido) complexes of Cu(II) and Ni(II) are difficult to prepare in pure form because they are hydrolyzed very easily in aqueous solution. Thus, Rising, *et al.*,[6] have found that the Cu(II) complex was invariably contaminated with the free ligand, and only poor analytical results could be obtained. Poddubnaya and Gabrilov[7] also noted the hydrolysis and decomposition of the Cu(II) complex in basic solution. The results of microanalyses of the Cu(II) and Ni(II) complexes reported by Kuroda, *et al.*,[3] were also not completely satisfactory.

In this paper we report a procedure for preparing pure oxamido complexes which are free from unreacted oxamide. We also report the infrared spectra of bis(oxamido) complexes of Cu(II), Ni(II), and Pd(II) from 4000 to 200 cm^{-1} and the results of a normal coordinate analysis of the Ni(II) complex including its deuterio and N^{15} analogs.

Experimental Section

Preparation of Compounds. (a) **Nondeuterated Complexes.**—Hoffman and Ehrhardt[2] prepared the Cu(II) and Ni(II) complexes in water at high alkali concentration. Under these conditions it is almost impossible to prepare the complex in pure form, both because oxamide decomposes partially and because the compound obtained is contaminated with ligand formed by the hydrolysis of the complex. It was found that dimethyl sulfoxide (DMSO) dissolves about 1 g of oxamide/100 ml of solvent at 60–70°. Therefore, we have prepared the oxamido complexes using DMSO as a solvent.

A 1-g amount of oxamide is mixed with a stoichiometric quantity of the metal nitrate or chloride. The mixture is then ground in a mortar and placed in 100 ml of DMSO. It is not necessary to dissolve all of the oxamide; a suspension of the material is suitable. KOH (50% in excess of that needed to form the metal hydroxide) is dissolved in 10 ml of water, and this is added dropwise with constant stirring to the suspension. The salt precipitates out and may then be filtered and washed with absolute ethanol. To purify the salt further, it is suspended in DMSO at 60 to 70°, then filtered and washed with dry acetone. This step is repeated two or three times. Drying of the salts may be carried out in a vacuum desiccator over P_2O_5. The Cu(II), Ni(II), and Pd(II) salts are rose-red, yellow, and white, respectively. Their composition was checked by analysis.

Anal. Calcd for $K_2Cu(C_2H_2N_2O_2)_2$: Cu, 20.25; C, 15.31; H, 1.28; N, 17.86. Found: Cu, 19.90; C, 15.58; H, 1.56; N, 17.58.

Anal. Calcd for $K_2Ni(C_2H_2N_2O_2)_2$: Ni, 18.93; C, 15.54; H, 1.30; N, 18.12. Found: Ni, 18.63; C, 15.41; H, 1.85, N, 17.84.

Anal. Calcd for $K_2Pd(C_2H_2N_2O_2)_2$: Pd, 29.83; C, 13.47; H, 1.13; N, 15.71. Found: Pd, 29.63; C, 13.20; H, 1.49; N, 15.41.

(b) **Deuterated Complexes.**—Oxamide-d_4 was prepared by bubbling ND_3 gas (purchased from Merck Sharp and Dohme of Canada, Ltd., Montreal) into a solution of diethyl oxalate in D_2O at 0°. The deuterated oxamide which precipitated was filtered and dried over P_2O_5. The hydrated metal nitrate or

---

[1] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965. This work was supported by a research grant, GM-10072-02, from the National Institutes of Health, Public Health Service. P. X. A. was supported by a National Science Foundation Grant under the Research Participation Program for College Teachers.

[2] K. A. Hoffmann and U. Ehrhardt, *Ber.*, **46**, 1457 (1913).

[3] Y. Kuroda, M. Kato, and K. Sone, *Bull. Chem. Soc. Japan*, **34**, 877 (1961).

[4] H. C. Freeman, J. E. W. L. Smith, and L. C. Taylor, *Nature*, **184**, 707 (1959).

[5] K. Aida, Y. Musya, and S. Kinumaki, *Inorg. Chem.*, **2**, 1268 (1963).

[6] M. H. Rising, J. S. Hicks, and G. A. Moarke, *J. Biol. Chem.*, **89**, 1 (1930).

[7] N. S. Poddubnaya and N. I. Gabrilov, *Zh. Obshch. Khim.*, **18**, 1848 (1948).

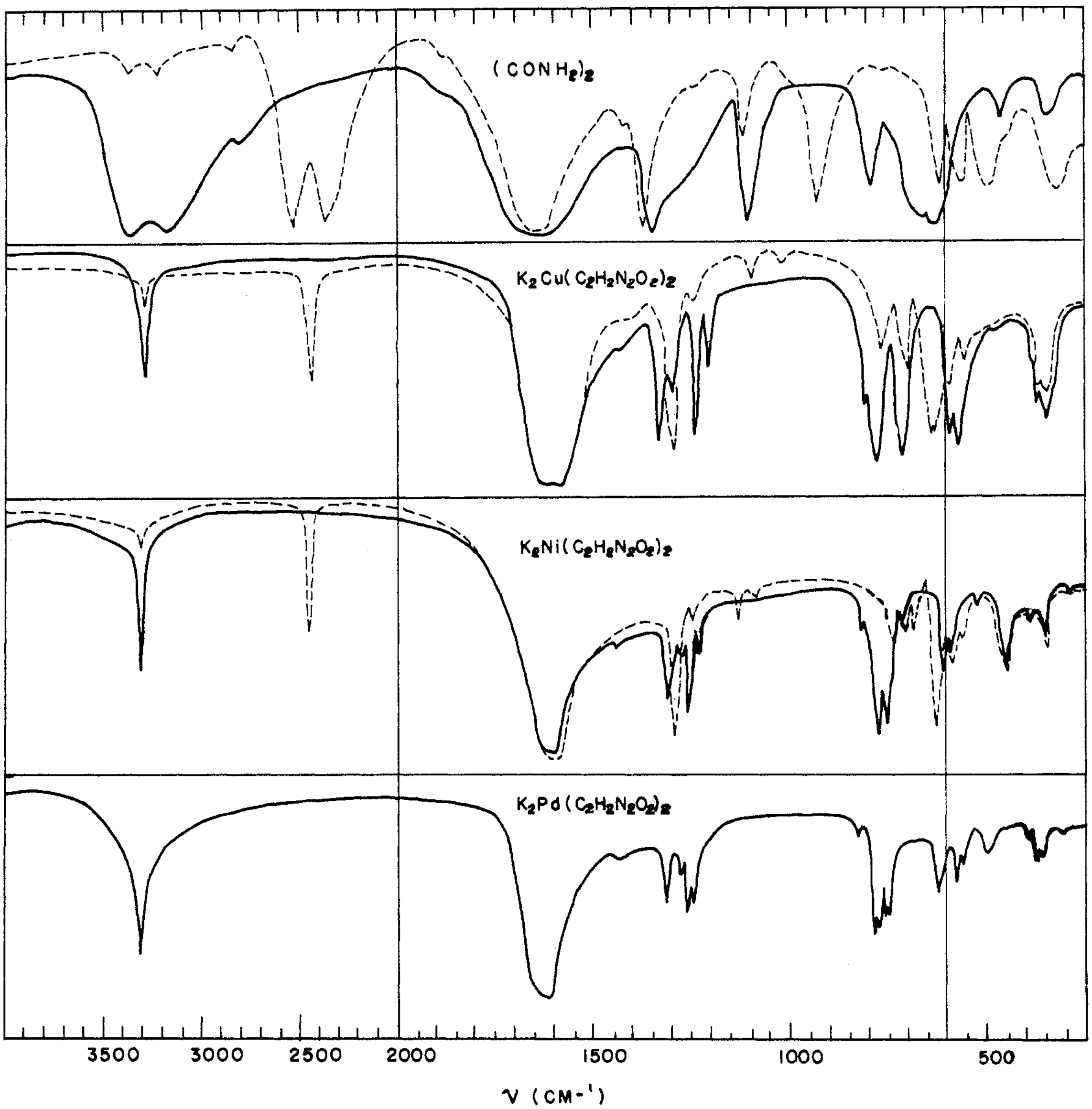


Figure 1.—Infrared spectra of oxamide and its metal complexes (dotted lines are for deuterio analogs).

chloride was dissolved in D_2O, placed in a closed tube, and allowed to stand for 3 to 4 days. The salts were reprecipitated in the cold and dried. This procedure was repeated two or three times to ensure complete deuteration. The deuterated Cu(II) and Ni(II) complexes were prepared from these deuterated reagents using the same method as used for the preparation of the nondeuterated complexes.

(c) **N^{15}-Substituted Ni Complex.**—$N^{15}H_3$ gas (obtained from Merck Sharp and Dohme of Canada, Ltd., Montreal) was transfered under vacuum to a solution of diethyl oxalate and water. The N^{15}-substituted oxamide which was precipitated from the solution was filtered, washed with acetone, and dried over P_2O_5. The Ni(II) complex was then prepared as described above.

Spectral Measurements.—A Perkin-Elmer Model 21 double-beam infrared spectrophotometer equipped with NaCl optics was used to obtain the spectra from 4000 to 700 cm^{-1}. Both the KBr-disk and Nujol-mull methods were used in this region. The spectrum from 700 to 200 cm^{-1} was obtained on Beckman Model IR-7 and IR-12 infrared spectrophotometers. The Nujol-mull technique with CsI plates was used in this region.

Infrared Spectra

Figure 1 illustrates the infrared spectra of oxamide, the potassium bis(oxamido) complexes of Cu(II), Ni(II), and Pd(II), and their deuterio analogs. Figure 2 compares the infrared spectra of the N^{14} and N^{15} species of bis(oxamido)nickel(II) complex. All of the observed frequencies are tabulated in Table I. The spectra of oxamide and its deuterio analog agree substantially with those reported previously by Scott and Wagner.[8] However, the spectra of the Cu(II) and Ni(II) complexes show a significant difference from those reported byKuroda, *et al.*;[3] bands reported near 1120 cm^{-1} for these complexes are completely missing in the present work. It is evident that these bands reported by Kuroda, *et al.*, are due to uncoordinated oxamide, which absorbs strongly at 1120 cm^{-1}. It is seen from Figure 1 that the infrared spectra of bis(oxamido) complexes of Cu(II), Ni(II), and Pd(II) are all alike in the NaCl region. This resemblance seems to suggest a similar structure for all these complexes. The two N–H stretching bands of oxamide at 3370 and 3200 cm^{-1} are replaced upon chelation by a sharp single band at about 3310 cm^{-1}. This change is similar to that observed for the N–H stretching bands

---

[8] T. A. Scott and E. L. Wagner, *J. Chem. Phys.*, **30**, 465 (1959).

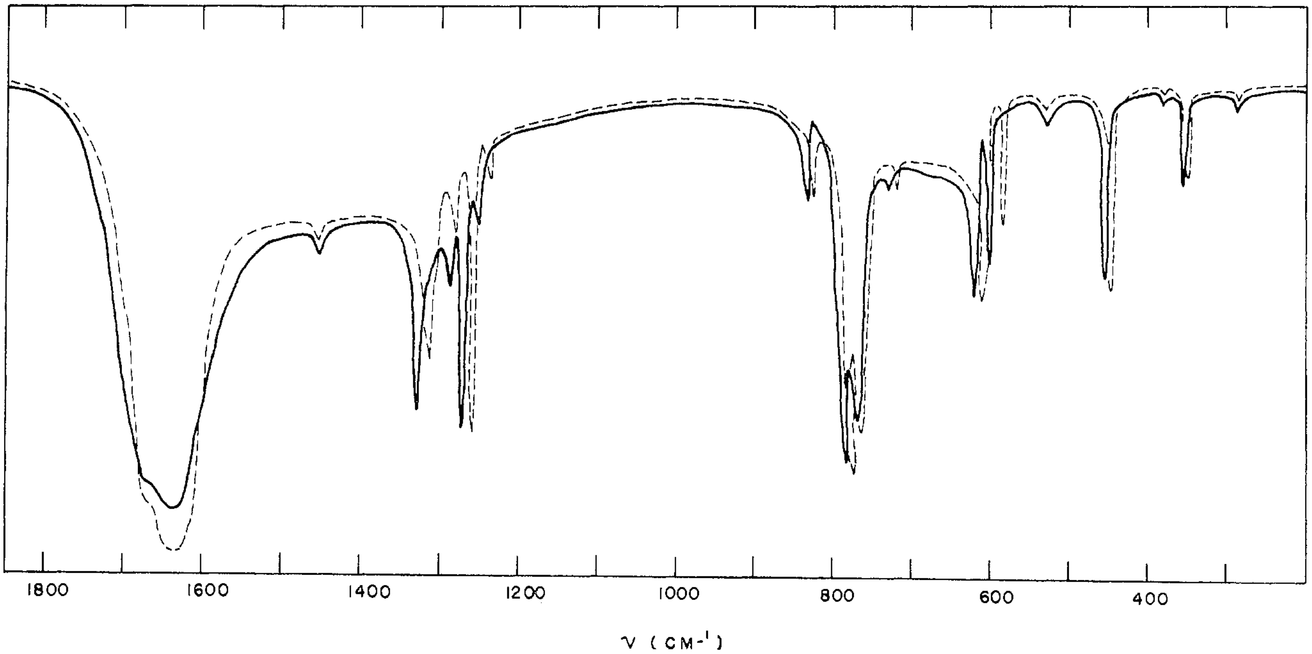


Figure 2.—Comparison of infrared spectra of bis(oxamido)nickel(II) complex and its N^{15}-substituted analog.

TABLE I

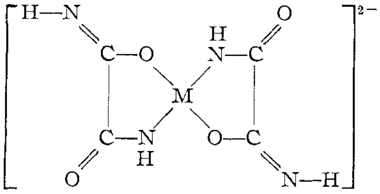
VIBRATIONAL FREQUENCIES OF BIS(OXAMIDO) COMPLEXES[a] (CM^{-1})

$K_2M(C_2H_2N_2O_2)_2$				K_2M-$(C_2D_2N_2O_2)_2$		Band assignment[b]
Ni	Ni (N^{15})	Cu	Pd	Ni	Cu	
3315	3310	3310	3310	2470	2460	$\nu(N—H)$, ν_1, ν_9
1660	1660	1620	1660	1660	1620	$\nu(C{=}O)$, ν_2, ν_{10}
1620	1620	1590	1620	1620	1590	
1440[c]	1435[c]	1435[c]	1420[c]	1435[c]	1430[c]	Combination band
1328	1315	1340	1320	1305	1305	$\nu(C—N)$, ν_3, ν_{11}
1268	1258	1250	1255	1250	1245	
1286	1280	1305	1287	1075	1100	$\delta(N—H)$, ν_4, ν_{12}
1250	1240	1215	1247	1040	1020	
834	825	815	830	755	770	$\nu(C—C)$, ν_5
785	775	780[d]	780 775	645	640	$\pi(N—H)$[e]
768	763	780[d]	767 757	700	655	$\delta(C{=}O)$, ν_{14}
725[c]	718[c]	725	...	717	715	?
625	615	600	618	605	610	$\pi(C{=}O)$[e]
603	590	575	580	575	550	
535[c]	530[c]	...	565	530[c]	...	Ring def, ν_{14}
458	453	473[c]	515	458	473	$\delta(C{=}O) + \nu(M—N)$, ν_6
385[c]	385[c]	(375)	385[c]	385[c]	(375)	
360	360	365 355	360	358	365 355	$\nu(M—N) + \delta(C{=}O)$, ν_7
290[c]	285[c]	310[b]	325[c]	290[c]	310[c]	$\nu(M—N)$, ν_{15}

[a] Values in parentheses indicate shoulders. [b] Band assignments for nondeuterated complexes. [c] Weak bands. [d] Overlap of two bands. [e] π denotes out-of-plane bending mode.

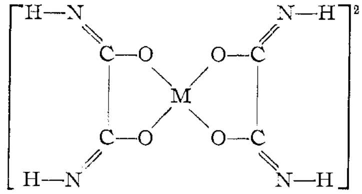
in going from primary to secondary amides[9] and is interpreted as an indication that one of the hydrogens of each NH_2 group is ionized upon coordination. A single band, or at most a closely spaced doublet, is observed for the N–H stretching mode of these complexes. This would preclude a structure such as II since two substantially different N–H stretching frequencies are expected for such a structure.

The strong broad doublet near 1660–1600 cm^{-1} is definitely due to the C=O stretching modes. It is

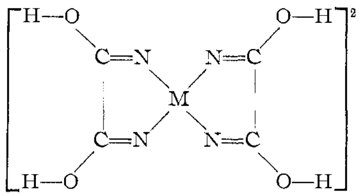


II

clear that these frequencies are too high to be assigned to either of the following structures



III



IV

Thus, it is concluded that the diimido structure (I) represents the most probable structure of the complex, as suggested earlier by Kuroda, *et al.*[3] Although the square-planar V_h structure (I) predicts only two infrared-active C–N stretching modes, Kuroda, *et al.*,[3] assigned all four bands between 1350 and 1200 cm^{-1} to the C–N stretching modes with the assumption that two other inactive modes may also be allowed because of relaxation of selection rules in the crystal lattice. We have found that two bands (a weaker pair at 1286 and 1250 cm^{-1} for Ni(II) and at 1305 and 1215 cm^{-1} for Cu(II)) disappear, while the two bands (a stronger pair at 1328 and 1268 cm^{-1} for Ni(II) and at 1340 and 1250

---

(9) L. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen Co., Ltd., London, 1958, p 203.

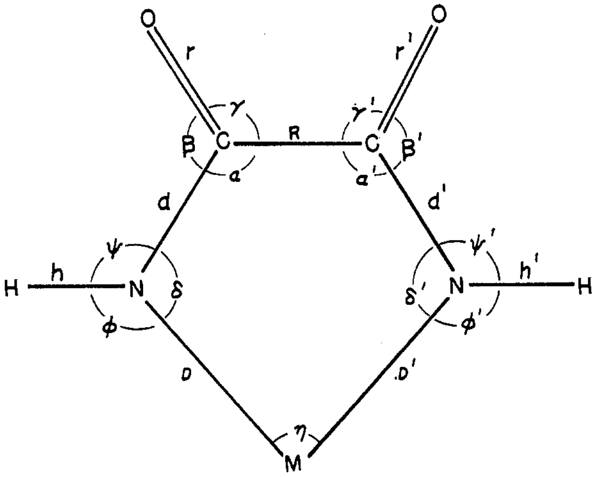


Figure 3.—Molecular model of 1:1 metal–oxamide complex.

cm^{-1} for Cu(II)) are shifted slightly upon deuteration. It is probable that the former two bands are due to the N–H in-plane bending modes and that the latter two are due to the C–N stretching modes.

The bands below 850 cm^{-1} are rather difficult to assign on an empirical basis. In order to give complete band assignments over the whole spectral region, we have carried out a normal coordinate analysis on the Ni(II) complex including its deuterio and N^{15} isotopic species.

Normal Coordinate Analysis

Since the square-planar diimido structure (I) seems to explain the observed spectra quite satisfactorily, we have carried out a normal coordinate analysis on this model. Although the spectra are obtained for 1:2 (metal:ligand) complexes, the analysis has been made on the 1:1 complex model shown in Figure 3. This approximation simplifies the calculations without introducing serious errors in frequencies and force constants.[10] Such an approximation is particularly appropriate for metal oxamido complexes since vibrational coupling between ligands is not serious in these weak chelates.

The 1:1 complex model of Figure 3 has 21 [(3 × 9) − 6] normal vibrations. With C_{2v} symmetry this model gives four classes into which these vibrations may be grouped. The in-plane vibrations ($8\ A_1 + 7\ B_2$) are separable from the out-of-plane vibrations ($3\ A_2 + 3\ B_1$). Only the 15 in-plane vibrations were calculated in this paper. We chose the 9 stretching and 13 angle-bending coordinates shown in Figure 3. The use of 22 internal coordinates for 15 vibrations leaves seven redundancies in our calculation. Five of these were removed by coordinate transformations (four concerned with the sum of the angles about the carbon and nitrogen atoms and one related to the sum of the five angles in the ring). The two remaining redundancies are not as readily removed and were left in the calculation. Table II lists the symmetry coordinates used in our calculations.

TABLE II

SYMMETRY COORDINATES FOR IN-PLANE VIBRATIONS

Species	Symmetry coordinate	Vibrational mode[a]
A_1	$S_1 = (1/\sqrt{2})(\Delta h + \Delta h')$	ν(N—H)
	$S_2 = (1/\sqrt{2})(\Delta r + \Delta r')$	ν(C=O)
	$S_3{}^b = (1/\sqrt{2})(\Delta\varphi - \Delta\psi + \Delta\varphi' - \Delta\psi')$	δ(N—H)
	$S_4 = (1/\sqrt{2})(\Delta d + \Delta d')$	ν(C—N)
	$S_5 = \Delta R$	ν(C—C)
	$S_6{}^b = (1/\sqrt{2})(\Delta\beta - \Delta\gamma + \Delta\beta' - \Delta\gamma')$	δ(C=O)
	$S_7 = (1/\sqrt{2})(\Delta D + \Delta D')$	ν(Ni—N)
	$S_8 = (1/2)(\Delta\delta + \Delta\delta' - \Delta\alpha - \Delta\alpha')$	Ring def
	$S_9 = (1/\sqrt{20})(4\Delta\eta - \Delta\delta - \Delta\delta' - \Delta\alpha - \Delta\alpha')$	Ring def
B_2	$S_{10} = (1/\sqrt{2})(\Delta h - \Delta h')$	ν(N—H)
	$S_{11} = (1/\sqrt{2})(\Delta r - \Delta r')$	ν(C=O)
	$S_{12}{}^b = (1/\sqrt{2})(\Delta\varphi - \Delta\psi - \Delta\varphi' + \Delta\psi')$	δ(N—H)
	$S_{13} = (1/\sqrt{2})(\Delta d - \Delta d')$	ν(C—N)
	$S_{14}{}^b = (1/\sqrt{2})(\Delta\beta - \Delta\gamma - \Delta\beta' + \Delta\gamma')$	δ(C=O)
	$S_{15} = (1/\sqrt{2})(\Delta D - \Delta D')$	ν(Ni—N)
	$S_{16} = (1/2)(\Delta\delta - \Delta\delta' + \Delta\alpha - \Delta\alpha')$	Ring def
	$S_{17} = (1/2)(\Delta\delta - \Delta\delta' - \Delta\alpha + \Delta\alpha')$	Ring def

[a] ν and δ denote stretching and bending modes, respectively.

[b] These coordinates are not normalized [see K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 538 (1960)].

The G-matrix elements were evaluated using the following molecular dimensions: $D = D' = 2.03$ A, $d = d' = 1.32$ A, $R = 1.40$ A, $r = r' = 1.28$ A, $h = h' = 1.02$ A, $\alpha = \alpha' = \beta = \beta' = \gamma = \gamma' = 120°$, $\delta = \delta' = 108°$, $\psi = \psi' = \phi = \phi' = 126°$, $\eta = 84°$. The F-matrix elements were expressed by using the simple Urey–Bradley force field.[11] Finally, two secular equations of the form $|GF - E\lambda| = 0$ were solved for the A_1 (ninth order) and B_2 (eighth order) species using an IBM 7094 computer. The fact that two "zero frequencies" are obtained, one for each species, provided a good check of our calculations.

Table III lists the set of force constants which gives the best fit to the observed frequencies for bis(oxamido)-nickel(II) and its deuterio and N^{15} isotopic species. Most of these force constants were transferred from those of bis(glycino)nickel(II) dihydrate[12] and were adjusted slightly to fit the present compounds. Table IV compares the observed frequencies with those calculated for the three isotopic species. The agreement is quite satisfactory; the average error for the 42 observed frequencies is 1.5% and maximum error is 4.1% (ν_{15} of the deuterated compound). The last column of Table IV gives the approximate description of each normal mode derived from the calculation of the potential energy distribution in each symmetry coordinate.[13]

TABLE III

FORCE CONSTANTS OF BIS(OXAMIDO)NICKEL(II) COMPLEX (MDYNES/A)

Stretching	Bending	Repulsion
K(Ni—N) = 0.73	H(N—Ni—N) = 0.02	F(N···N) = 0.02
K(C=O) = 8.80	H(C—C—N) = 0.30	F(C····N) = 0.05
	H(O=C—C) = 0.55	F(O····C) = 0.55
K(N—H) = 5.83	H(O=C—N) = 0.50	F(O····N) = 1.50
K(C—N) = 4.50	H(Ni—N—C) = 0.05	F(Ni····C) = 0.02
	H(H—N—C) = 0.10	F(H····C) = 0.53
K(C—C) = 2.50	H(H—N—Ni) = 0.23	F(H····Ni) = 0.08

As is seen in Table IV, the results of normal coordinate analysis confirm the previous empirical band

---

(10) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 331 (1962).

(11) T. Shimanouchi, *ibid.*, **17**, 245 (199).

(12) R. A. Condrate and K. Nakamoto, *ibid.*, **42**, 2590 (1965).

(13) Y. Morino and K. Kuchitsu, *ibid.*, **20**, 1809 (1952).

assignments in the region above 850 cm^{-1}. Vibrational coupling was found only in ν_{11} (1268 cm^{-1} of the nondeuterated species), which consists of the C–N stretching coupled with the N–H in-plane bending mode.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED FREQUENCIES FOR $K_2Ni(C_2H_2N_2O_2)_2$ AND THE DEUTERATED AND N^{15} ISOTOPIC SPECIES (CM^{-1})

	K_2Ni-$(C_2H_2N_2O_2)_2$		K_2Ni-$(C_2D_2N_2O_2)_2$		K_2Ni-$(C_2H_2N^{15}{}_2O_2)_2$		Band
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	assignment[a]
				A_1			
ν_1	3315	3352	2470	2446	3310	3345	ν(N—H)
ν_2	1620	1594	1620	1593	1620	1593	ν(C=O)
ν_3	1328	1342	1305	1337	1315	1333	ν(C—N)
ν_4	1286	1260	1075	1035	1280	1252	δ(N—H)
ν_5	834	842	755	740	825	831	ν(C—C)
ν_6	458	460	458	449	453	450	δ(C=O) + ν(M—N)
ν_7	360	355	358	352	360	353	ν(M—N) + δ(C=O)
ν_8	. . .	199	. . .	197	. . .	198	Ring def
				B_2			
ν_9	3315	3352	2470	2446	3310	3345	ν(N—H)
ν_{10}	1660	1695	1660	1694	1660	1693	ν(C=O)
ν_{11}	1268	1272	1250	1264	1258	1259	ν(C—N) + δ(N—H)
ν_{12}	1250	1251	1040	1000	1240	1249	δ(N—H)
ν_{13}	768	765	700	692	763	755	δ(C=O)
ν_{14}	535	555	530	546	530	546	Ring def
ν_{15}	290	281	290	278	285	277	ν(M—N)

[a] These band assignments were obtained from the calculation of the potential energy distribution for the nondeuterated species. The frequencies of the other isotopic species were arranged so that frequencies listed in the same row of the table correspond approximately to the vibrational mode given for the nondeuterated species.

The weak shoulder band at 834 cm^{-1} (ν_5) is assigned to the C–C stretching mode. Upon deuteration, this band is shifted to 755 cm^{-1} and couples strongly with the N–D in-plane bending mode. The band at 785 cm^{-1} is assigned to the N–H out-of-plane bending mode which is not calculated in this paper. It is interesting to note that the N–H in-plane and out-of-plane bending frequencies reported here are similar to those obtained for diformylhydrazine (1229 and 770 cm^{-1}, respectively).[14] The C=O in-plane bending frequency of this latter compound (753 cm^{-1}) is slightly lower than the N–H out-of-plane bending frequency (770 cm^{-1}). In accordance with this, the C=O in-plane bending frequency of the Ni(II) complex has been calculated to be 768 cm^{-1} (ν_{13}).

The doublet near 610 cm^{-1} of the Ni(II) complex is assigned to the C=O out-of-plane bending mode. A similar doublet has been observed for the Ni(II) glycolato complex near 575 cm^{-1} and assigned to the same mode.[15] The weak band at 535 cm^{-1} is assigned to one of the ring deformation modes (ν_{14}). A mode similar to this has been observed at 543 cm^{-1} for the Ni(II) glycolato complex.[15]

The bands at 458 and 360 cm^{-1} are both due to the coupled vibrations between C=O in-plane bending and Ni–N stretching modes (ν_6 and ν_7). A purer Ni–N stretching mode (ν_{15}) is observed at 290 cm^{-1} as a weak band. It is seen in Table I that both ν_6 and ν_{15} are metal sensitive and seem to shift progressively to higher frequencies as the metal is changed in the order Ni(II) < Cu(II) < Pd(II). This result suggests that the strength of the metal–nitrogen bond in oxamido complexes increases in the above order of metals. It is noted that the ν_6 frequencies obtained for the oxamido complexes (458 cm^{-1} for Ni(II), 473 cm^{-1} for Cu(II), and 515 cm^{-1} for Pd(II)) are similar to those observed for metal–nitrogen stretching frequencies of the corresponding glycino complexes (439 cm^{-1} for Ni(II), 481 cm^{-1} for Cu(II), and 550 cm^{-1} for Pd(II)[12]). The Ni–N stretching force constant of the oxamido complex (0.73 mdyne/A) is also similar to that found for the glycino complex (0.70 mdyne/A). It is therefore concluded that the strength of the Ni–N bond is almost the same in these complexes.

Acknowledgments.—The authors express their appreciation and thanks to the personnel of the Argonne National Laboratory for permission to use their IR-7 infrared spectrophotometer. We are also grateful to Mr. H. Ogoshi and Mr. Alec E. Bridges for technical assistance.

---

(14) T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).

(15) K. Nakamoto, P. J. McCarthy, and B. Miniatas, *Spectrochim. Acta*, **21**, 379 (1965).