Infrared Spectra and the Structure of Some Metal-oxamide Complexes

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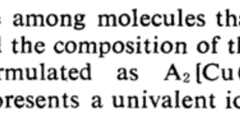
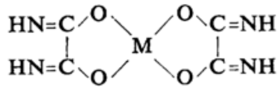
Many kinds of proteins, polypeptides and biuret-like compounds react with Cu^{2+} ions in basic solutions, forming chelate complexes with characteristic red or violet colors ("biuret reaction")[1-4]. Oxamide is known to be the simplest one among molecules that exhibit this reaction, and the composition of the red product can be formulated as $A_2[Cu(C_2H_2N_2O_2)_2]$, where A represents a univalent ion (e. g. alkali metal ion). It is also known that Ni^{2+} ions form a yellow complex of analogous composition[5,6].

Although the formula of these complexes and the reported diamagnetism of the nickel complex[7] afford some evidence in favor of the presumption that these complexes are tetra-coordinated chelates, their structure has not yet been established definitely***. The reason is as follows: An oxamide molecule contains two nitrogen and two oxygen atoms capable of forming coordinate bonds with a metal, while the constitution of a tetra-coordinated complex with a bivalent central ion does not permit all these atoms to be involved in metal-ligand linkages. This situation makes a number of structures conceivable, e. g.,



(I)

(II)



(III)

etc., among which the formula I seems to be more probable than the others, because of the analogy of the color and general mode of formation of these complexes with those of biuret complexes of the corresponding metals[1-4].

In connection with this problem, it can be expected that infrared spectroscopy will provide a powerful means for the determination of the kind of donor atoms in these complexes, and the elucidation of their geometric structure. In this paper, the infrared absorption spectra of $K_2[Ni(C_2H_2N_2O_2)_2]$ and $K_2[Cu(C_2H_2N_2O_2)_2]$ are reported and discussed from this point of view.

Experimental Procedure and Results

Materials. — Potassium bis(oxamido)niccolate(II) and potassium bis(oxamido)cuprate(II) were prepared by the method of Hofmann and Ehrhardt[6]. and dried over potassium hydroxide.

Found: Ni, 18.1; N, 16.8. Calcd. for $K_2[Ni(C_2H_2N_2O_2)_2]$: Ni, 19.0; N, 18.1%.

Found: Cu, 18.5; N, 17.4. Calcd. for $K_2[Cu(C_2H_2N_2O_2)_2]$: Cu, 20.2; N, 17.9%.

A specimen of oxamide, $C_2H_4N_2O_2$, was obtained from L. Light & Co. Ltd.

Measurements. — The infrared spectra were recorded by means of a Hilger H-800 spectrophotometer. The absorption measurements were made at room temperature using pressed potassium bromide disk technique in the wave number range from 700 to 4000 cm^{-1} with a rock-salt prism. A fluorite prism was also used for a range above 1200 cm^{-1}, but no additional information was obtained. The results were checked using Nujol mulls. The spectra obtained are shown in Fig. 1, and the observed frequencies of the absorption bands are listed in Table I. The present data on oxamide are in good agreement with those reported by Miyazawa[8] and by Scott and Wagner[9].

Discussion

A close resemblance exists between the absorption patterns of the metal complexes, indicating that they have a similar structure. On

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[1] G. Wiedemann, *Ann.*, **68**, 323 (1848).

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[5] H. Schiff, *Ann.*, **299**, 236 (1898).

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

[7] L. Cambi and E. Tremolada, *Gazz. chim. ital.*, **65**, 322 (1935).

*** The recent X-ray studies by Freeman et al. (H. C. Freeman, J. E. W. L. Smith and J. C. Taylor, *Nature*, **184**, 707 (1959).) on the structure of bis(biureto)cuprate(II) is of interest in connection with this study.

[8] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 86 (1954).

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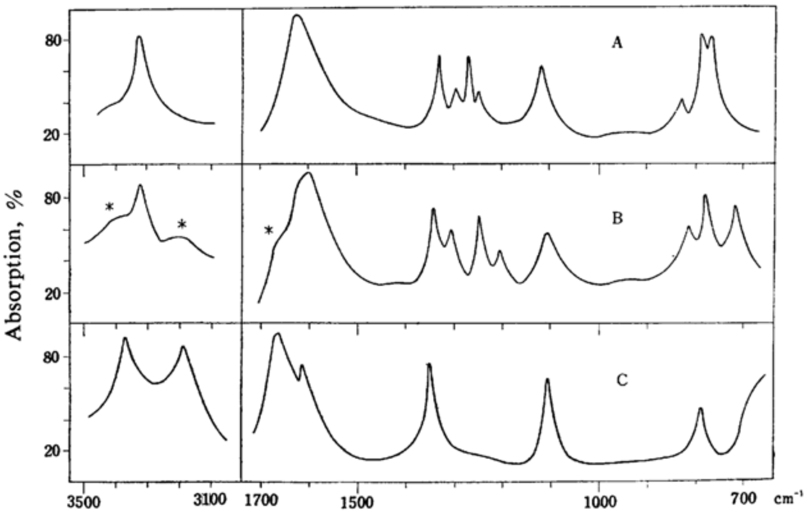

Fig. 1. The infrared spectra of (A): potassium bis(oxamido)niccolate(II), (B): potassium bis-(oxamido)cuprate(II), and (C): pure oxamide. The peaks marked with an asterisk seem to be due to the contamination of oxamide[2)] produced by the decomposition of the easily hydrolyzable copper complex, because their positions coincided with those of the strong absorption bands of oxamide and their intensity increased considerably after the complex was exposed to atmospheric moisture.

TABLE I. OBSERVED INFRARED ABSORPTION FREQUENCIES IN cm^{-1}

$K_2[Ni(C_2H_2 \cdot N_2O_2)_2]$	$K_2[Cu(C_2H_2 \cdot N_2O_2)_2]$	Assignment
3320 (s)	3313 (s)	ν_{N-H}
1628 (vs)	1600 (vs)	$\nu_{C=O}$
1325 (m)	1343 (m)	ν_{C-N}
1285 (w)	1305 (w)	
1268 (m)	1253 (m)	
1250 (w)	1215 (w)	
1124 (m)	1120 (m)	ρ_{N-H}
831 (w)	815 (w)	ν_{C-C}
786 (s)	788 (s)	ω_{N-H}
765 (s)	722 (s)	$\rho_{C=O}$

Absorption intensities are shown by letters in parentheses, i. e., vs: very strong, s: strong, m: medium, w: weak.

Vibrational types are expressed by greek letters, i. e., ν: stretching, ρ: in-plane deformation, ω: out-of-plane deformation.

the other hand, the feature of these spectra is much different from that of an oxamide molecule. It has revealed that heavy atoms in an oxamide molecule are arranged in a trans (C_{2h}) form in solid state[8,9)]. However, it is unbelievable that an oxamide molecule having the trans form can act as a bidental ligand, provided that the coordination takes place through one kind of donor atoms. A more complicated spectral feature of the metal complexes probably reflects a less symmetrical structure of the ligand. The complication of the spectra should partly be caused by vibrational couplings between two ligands through coordination linkages. This effect is expected to be more appreciable for the vibrational modes of groups directly attached to the metal than for those of end groups.

In the first place, a remarkable difference between the spectra of an oxamide molecule and those of the metal complexes was found in the region from 3100 to 3400 cm^{-1}. The former show two strong bands arising from the N-H stretching vibrations of primary amide groups, O=C-NH_2, while the latter show only one peak. This fact means that the primary amide structure is absent in these metal complexes. Another evidence in favor of the absence of an NH_2 group in metal complexes is provided by a spectral feature in the wave number range near 1600 cm^{-1}. For an oxamide molecule, the NH_2 bending frequency was found at 1610 cm^{-1}, whereas the corresponding band is absent in the spectra of the metal complexes. The values of 3320 cm^{-1} for the nickel complex and of 3313 cm^{-1} for the copper complex are reasonable for the N-H stretching frequencies of secondary amides in solid state[10)], although there still remains a possibility of assigning them to the frequency of hydrogen-bonded OH groups. This ambiguity of assignment for these frequencies can be removed by examining the C=O stretching

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10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., Methuen, London (1958), p. 205.

band. If the metal complexes take a structure having OH groups, such as II, an intense absorption at about 1600 cm^{-1} characteristic of C=O bonds should be replaced by a C=N stretching band which is generally less intense than a C=O band. But this was not the case. In this region, both of the metal complexes show a band of nearly the same intensity as the C=O stretching band of an oxamide molecule. Therefore, the band at about 3320 cm^{-1} of the metal complexes was assigned unequivocally to the N–H stretching vibration.

Also the characteristic C=O band above 1600 cm^{-1} is expected to disappear from the spectra of metal complexes, if the ligands were coordinated to the metal through oxygen atoms (structure III), since it can be reasonably presumed that the formation of metal-oxygen bonds will cause a shift in the C=O stretching band to a much lower frequency owing to the decreasing double bond character of the C=O group. Moreover the CO bonds incorporated in a five-membered chelate ring will have no longer the character of end groupswhich display a simple absorption band, so that the appearance of the absorptions is expected to be greatly complicated because of coupling with other skeletal vibrations. Therefore, the presence of a simple C=O band in the spectra of metal complexes may be taken as sufficient evidence for the fact that these complexes have metal-nitrogen bonds rather than metal-oxygen bonds.

The value of 1628 cm^{-1} for the nickel complex and that of 1600 cm^{-1} for the copper complex are slightly lower than the value of 1660 cm^{-1} for the C=O frequency of an oxamide molecule, indicating the decreased double bond character of the C=O bonds in the coordinated ligands. This effect is certainly due to the increased ionic character of such ligands, because the metal-nitrogen bonds are expected to have only a partial covalent character. It is of interest to note that the infrared spectra of the oxalate complexes of bivalent metals, $[M^{II}(C_2O_4)_2]^{2-}$, bear a close resemblance to this case[11]. The carboxylate frequencies of these complexes are intermediate between those of the oxalates of alkali metals and those of dimethyl oxalate, suggesting a partial covalent character of their metal-oxygen bonds. The fact that the observed frequency of the C=O stretching vibration of the nickel complex is higher than that of the copper complex indicates that the metal-nitrogen bonds of the former have a greater covalent character than those of the latter.

The spectral changes caused by the formation of the metal complexes are most apparent in the wave number range from 1350 to 1200 cm^{-1}. An oxamide molecule has a strong absorption band at 1355 cm^{-1} arising from the C–N stretching vibration, while the metal complexes exhibit four peaks, two of which are of medium intensity and others are weak. It can be expected that the C–N stretching frequencies of the metal complexes will also appear in this region, since the double bond character of these bonds should not be affected so much on substitution of the hydrogen atoms of the NH_2 groups with a metal atom. However, the absorption feature will be complicated by vibrational coupling through the metal-nitrogen linkages. The spectral pattern in this region must therefore depend on the geometric structures of these complexes.

Conceivable models for these complexes are as follows. (1) A planar structure in which four metal-nitrogen bonds as well as all the heavy atoms of the two ligands lie on a plane (D_{2h}). (2) Structures in which the coordination type is planar and each ligand takes a non-planar form, owing to a rotation about a C–C single bond from the cis configuration. Depending on the relative orientation of two ligands, two forms are conceivable, one of which has a center of symmetry (C_{2h}) while the other has not (D_2). (3) One form of tetrahedral chelation of two planar ligands (D_{2d}). (4) Two forms of tetrahedral chelation of two non-planar ligand (D_2 and C_2).

Selection rules operating on these models are summarized in Table II. These rules should hold rather strictly in the skeletal vibrations such as C–C and C–N vibration, while the end groups are presumed to be free from these. Actually, no splitting was observed for the N–H and C=O stretching bands of the metal complexes.

For the C–N stretching vibration, D_{2h} and C_{2h} models have two infrared active modes and two inactive ones. A D_{2d} model has two active modes, one of which is degenerate, and an inactive one. A D_2 model has three active ones and an inactive one. With a model having C_2 symmetry, all four modes are active. The four bands observed in this wave number region readily permit one to exclude the D_{2d} and D_2 models. However, it is difficult for other models (D_{2h}, C_{2h} and C_2) to decide which is the closest one to the actual structure, because these selection rules are valid only for a free molecule and the removal of prohibition can be expected to some extent in the solid state, for which intermolecular or interlattice effects should not be ignored. Therefore, there is a possibility of assigning these two weak bands to the inactive modes of the D_{2h} or C_{2h} model.

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[11] M. J. Schmelz, T. Miyazawa, S. Mizushima, T. J. Lane and J. V. Qaugliano, *Spectrochim. Acta*, 9, 51 (1957).

TABLE II. CLASSIFICATION OF VIBRATIONAL TYPES FOR CONCEIVABLE MODELS OF $[M^{II}(C_2H_2N_2O_2)_2]^{2-}$

	D_{2h}	C_{2h}	D_{2d}	D_2	C_2
ν_{N-H} $\nu_{C=O}$ ν_{C-N} ρ_{N-H} $\rho_{C=O}$	A_{1g}(R)	A_g(R)	A_1(R)	A_1(R)	2A(R, I)
	B_{1u}(I)	A_u(I)	B_2(R, I)	B_1(R, I)	
	B_{2g}(R)	B_g(R)	E(R, I)	B_2(R, I)	2B(R, I)
	B_{3u}(I)	B_u(I)		B_3(R, I)	
ν_{C-C}	A_{1g}(R)	A_g(R)	A_1(R)	A_1(R)	2A(R, I)
	B_{1u}(I)	B_u(I)	B_2(R, I)	B_1(R, I)	
ω_{N-H}	A_{1u}(ia)	A_u(I)	B_1(R)	A_1(R)	2A(R, I)
	B_{1g}(R)	A_g(R)	A_2(ia)	B_1(R, I)	
	B_{2u}(I)	B_u(I)	E(R, I)	B_2(R, I)	2B(R, I)
	B_{3g}(R)	B_g(R)		B_3(R, I)	

The meaning of letters in parentheses are as follows; R: Raman active, I: Infrared active, ia: inactive in both.

On the other hand, it has been revealed from a magnetic study⁷⁾ that the nickel complex is diamagnetic and hence tetrahedrally chelated structures are unlikely. Furthermore, it is possible that the π electron systems of the four amide groups give rise to some extent of conjugation effects through the d_π orbitals of the central metal, and if such effects are taken into account, the planar form (D_{2h}) seems to be the most probable among the possible models. The whole spectra of these complexes are satisfactorily interpreted in terms of the structure I with a D_{2h} symmetry, although there is an alternative possibility that the symmetry may be of C_{2h}.

Bands of the nickel complex at 831 cm^{-1} and of the copper complex at 815 cm^{-1} have no counterpart in the spectra of oxamide, but the frequencies are very close to a Raman frequency 800 cm^{-1} ascribed to the C–C stretching vibration of oxamide⁸⁾. The position and the weak intensity of these bands give a good evidence for assigning them to the C–C stretching mode.

Other frequencies expected to appear in the rock-salt region are the in-plane N–H deformation, the out-of-plane N–H deformation and the in-plane C=O deformation. According to general knowledge, the first has the highest frequency among them. Therefore, a band of the nickel complex at 1124 cm^{-1} and a band of the copper complex at 1120 cm^{-1} were assigned to this vibration. Two other bands of the nickel complex at 786 and 765 cm^{-1} as well as those of copper complex at 788 and 722 cm^{-1} were tentatively assigned to the out-of-plane N–H deformation and the in-plane C=O deformation, respectively. These assignments seem to be adequate, because in *N*-monosubstituted amides, it was found that the frequency of the former vibration is higher and its intensity is larger than those of the latter¹²⁾; for example, the former is assigned to 778 cm^{-1} and the latter to 765 cm^{-1} in the case of *N, N'*-dimethyloxamide, which was examined by studying the deuteration effect¹³⁾.

These assignments are also listed in Table I.

Summary

The infrared absorption spectra of potassium bis(oxamido)niccolate(II) and potassium bis(oxamido)cuprate(II) were recorded in the wave number region from 700 to 4000 cm^{-1} and compared with those of pure oxamide. These spectra revealed that metal-nitrogen bonds are formed in these complexes. The observed frequencies were interpreted in terms of a planar structure having the symmetry D_{2h}.

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12) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 526 (1956).

13) T. Miyazawa, ibid., **76**, 1018 (1955).