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Reactions of Nickel(II), Copper(II) and Palladium(II) Complexes of Bis(acetylacetone)ethylenediimine with Nitric Oxide

Isao Masuda, Motonori Tamaki and Koichiro Shinra

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada, Suita, Osaka

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Through reaction with nitric oxide, divalent Ni, Cu, and Pd complexes of bis(acetylacetone)-ethylenediimine have been shown to yield fine crystalline compounds of the general formula $M(C_{12}H_{17}N_3O_3)$, where M=Ni or Cu, and of $M(C_{12}H_{16}N_4O_4)$ where M=Ni, Cu or Pd, depending on experimental conditions. They are insoluble in water. The former compounds are rather soluble in common organic solvents, but the latter are sparingly soluble, except in pyridine. On the basis of analytical data and IR-spectral analyses, they are thought not to be nitrosyl metal-complexes but oxime type complexes.

It is well known that the γ-H of metal acetylacetonates can be replaced by halogens or nitro groups.[1] However, the reactivity of chelate complexes, such as acetylacetonate, towards nitric oxide is not yet clarified. In this connection, only a few examples are found in the following studies. Djordjenič *et al.*[2] reported that through reaction with nitrosyl chloride in benzene, platinum(II) acetylacetonate yields a γ-chlorosubstituted compelx, whereas nickel(II) complex yields a compound which is thought to be either an oxime or a nitroso compound. By reaction with nitrite ions in the presence of ammonia, nickel(II) and palladium(II) complexes of acetylacetone yield a compound thought to be a γ-nitroso substituted complex, as shown in Fig. 1. On the other hand, it was shown by Nast *et al.*[3] that cobalt(II) acetylacetonate reacts with nitric oxide to yield a nitrosyl complex, CoA_2*[1](NO), in which nitric oxide is bonded to the central metal.

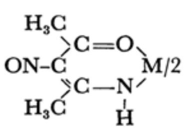

Fig. 1. M=Ni(II); Pd(II)

In the present work, nickel(II), copper(II) and palladium(II) complexes of bis(acetylacetone)ethylenediimine, which have metal-chelate rings analogous to that of acetylacetonate are reported to react with nitric oxide in organic solvents to form new complexes which are thought to have the structures shown in Figs. 2 and 3.

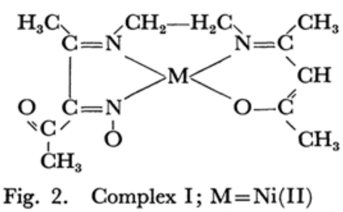

Fig. 2. Complex I; M=Ni(II)
Complex III; M=Cu(II)

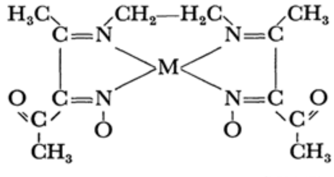

Fig. 3. Complex II; M=Ni(II)
Complex IV; M=Cu(II)
Complex V; M=Pd(II)

Experimental

Materials. Metal complexes of bis(acetylacetone)-ethylenediimine used in the reactions with nitric oxide were prepared according to McCarthy *et al.*[4] NiAE*[2] was purified by recrystallization from an 80% aqueous acetone solution, then dried at 100°C, obtaining reddish brown crystals. CuAE, recrystallized from acetone, was dried at 100°C, yielding dark violet crystals. PdAE, recrystallized from benzene, was dried at 100°C, yielding yellow crystals.

Nitric oxide was generated by the reaction of copper with aqueous nitric acid, and purified by passage through aqueous sodium hydroxide and a tower containing pellets of sodium hydroxide.

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1) J. P. Collman, "Reactions of Coordinated Ligands," Am. Chem. Soc., New York (1960), p. 78.

2) C. Djordjevič, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, **1962**, 4778.

3) R. Nast and H. Bier, *Ber.*, **92**, 1858 (1959).

*[1] A represents acetylacetonato.

4) P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1950).

*[2] AE represents bis(acetylacetone)ethylenediiminato.

TABLE 1. ELEMENTAL ANALYSES OF THE COMPLEXES

Formula	Complex	Cacld %				Found %			
		Metal	C	H	N	Metal	C	H	N
$NiC_{12}H_{17}N_3O_3$	I	18.9	46.35	5.83	13.50	18.7	46.35	5.53	14.06
$NiC_{12}H_{16}N_4O_4$	II		42.52	4.76	16.53		42.59	5.01	16.79
$CuC_{12}H_{17}N_3O_3$	III		45.40	5.71	13.24		45.54	5.52	13.88
$CuC_{12}H_{16}N_4O_4$	IV		41.92	4.69	16.29		41.99	4.69	16.22
$PdC_{12}H_{16}N_4O_4$	V	27.5	37.30	4.17	14.45	28.4	37.18	4.59	14.20

Reactions with Nitric Oxide. NiAE: 2.0 g of NiAE was dissolved in 100 *ml* of chloroform, and nitric oxide bubbled through the ice-cooled solution for about fifty minutes until the reddish-brown color of the solution turned to red. Then, the nitric oxide in the solution was driven off by bubbling nitrogen gas through the solution. The orange precipitate was filtered off, and the filtrate evaporated *in vacuo* to leave a red solid. The precipitate was recrystallized from methanol or toluene to give fine red crystals (complex I). The results of elementary analysis, given in Table 1, correspond to the formula shown in Fig. 2. The molecular weight determined with an ebulliometer in toluene for a 0.02 M solution was 298, showing the complex to be monomeric.

Using dichloromethane as a solvent, and bubbling nitric oxide through the solution for 30—40 min, an orange complex precipitated. The precipitate was recrystallized by dissolving it in a large volume of boiling dichloromethane and then cooling the solution. Fine orange crystals (complex II) were obtained. The results of elementary analysis, given in Table 1, correspond to the formula shown in Fig. 3. The orange complex differed from the red complex that was obtained through reaction in chloroform and was only slightly soluble in most organic solvents. It is stable in pyridine, and the complex that was obtained from pyridine solution after the solution was boiled for three hours gave the same infrared spectrum as that of the original orange complex.

CuAE: Two grams of CuAE were dissolved in 100 *ml* of chloroform, and air expelled from the solution and reaction flask by bubbling in nitrogen. Then the ice-cooled solution was saturated with nitric oxide by passing the gas through it for about 20 min. Stirring the solution in air for 20—30 min changed its color from violet to dark red-violet. The solution was evaporated *in vacuo*, leaving a precipitate, which was washed with ether to remove unreacted CuAE. It was recrystallized by dissolution in 50 *ml* of hot methanol and then cooling. Dark red-violet crystals (complex III) were obtained. The analytical results given in Table 1 indicate the formula shown in Fig. 2.

When nitrogen oxide was bubbled through the chloroform solution of CuAE in a similar way as mentioned above, for about two hours, a brown colored complex precipitated. The precipitate was filtered off, washed with chloroform and air-dried. It was recrystallized from methanol to give yellowish-brown crystals (complex IV). The complex was less soluble in most organic solvents than the red complex; analysis indicates the formula shown in Fig. 3.

PdAE: 0.2 g of PdAE dissolved in 50 *ml* of benzene was reacted with nitrogen oxide in the same way as above. After bubbling in nitric oxide for 30—50 min, the solution changed in color from yellow to orange, and an orange complex precipitated. The precipitate was filtered off and washed with benzene and then ether. Recrystallization from dichlorobenzene or pyridine gave fine orange crystals (complex V). Elementary analysis indicated the formula shown in Fig. 3.

Infrared Spectra. Infrared spectra were measured in KBr using a Shimadzu IR-27C spectrometer in the 650—4000 cm^{-1} region. Spectra in the 250—700 cm^{-1} region were obtained in KBr with an Hitachi EPI-L spectrometer.

Results and Discussion

Elementary analyses show that complexes II, IV and V have compositions which correspond to compounds with metal-AE : NO molecular ratios of 1 : 2. As for complexes I and III, analysis indicates a metal-AE: NO molecular ratio of 1 : 1. The solubilities of the complexes, their being insoluble in water and soluble in common organic solvents, suggest that they are non-ionic.

In order to formulate the complexes, their infrared spectra were examined. As is seen in Figs. 6—8, complexes II, IV and V display quite similar spectra, indicating similar structures.

It is well known that metal complexes of AE[5] or β-ketoamine,[6] which have unsaturated, six-membered metal chelate rings, such as shown in Fig. 4, are characterized by two or three absorption bands with strong intensities in the 1500—1600 cm^{-1} region, and the band due to π_{C-H} at about 760 cm^{-1}. Compared with this, the spectra of complexes II, IV and V are conspicuous by the absence of strong bands in the 1500—1600 cm^{-1} region and the band due to π_{C-H} (Figs. 6—8). However, the complexes exhibit strong bands in

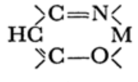

Fig. 4

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[5] K. Ueno and A. E. Martell, *J. Am. Chem. Soc.*, **59**, 998 (1955).

[6] H. F. Holtzclaw, J. P. Collman and R. M. Alire, *ibid.*, **80**, 1100 (1958); R. D. Archer, *Inorg. Chem.*, **2**, 292 (1963).

a higher wave number region, 1660—1689 cm^{-1}. The new bands are attributed to the stretching frequencies of N=O, C=O or C=N from general considerations of their positions and intensities. But in the case of these complexes, the absence of the strong bands in the 1500—1600 cm^{-1} region is thought to eliminate a formula where an N=O group is bound to the γ-C (Fig. 4) on the chelate rings of the original metal-AE, though the π_{C-H} band apparently disappeared. Since in the spectra of metal acetylacetonates, bands analogous to those of metal-AE in the 1500—1600 cm^{-1} region are known not to vanish by substitution on γ-C of an unsaturated group such as nitro-, phenyl- or formyl-groups.7) A nitrosyl type of structure is also discarded for the following reason. Nitrosyls of nickel, copper and cobalt complexes with AE, where the NO group is bound to the central metal, were synthesized by another method.8) Their spectra show strong bands at about 1680 cm^{-1}, which resemble in position the bands at 1660—1689 cm^{-1} obtained for complexes II, IV and V. However, in the case of these nitrosyls, they still retain the strong 1500—1600 cm^{-1} bands that are diagnostic of the parent metal-AE, and also retain the π_{C-H} band at about 760 cm^{-1}.

Thus, the evidences described above reject the most probable structures containing NO groups in the complexes. A considerably different skeleton for the structures of the complexes from that of the original metal-AE is then proposed. The spectrum of tris(isonitrosoacetylacetonato)Co(III) was inspected and compared with that of the complexes. Co(INA)$_3$[*3] has been formulated as shown in Fig. 5,9) and its spectrum given in Fig. 9 has no strong band in the 1500—1600 cm^{-1} region except

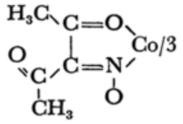
Fig. 5

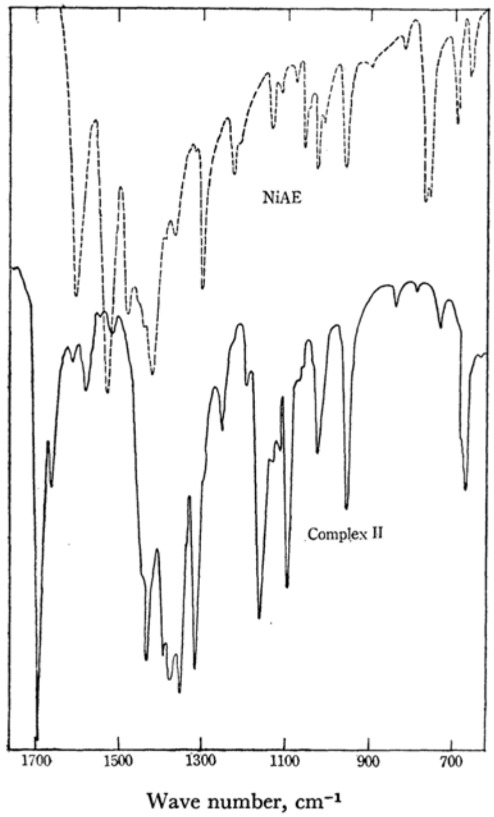

Fig. 6. IR spectra of NiAE and complex II.

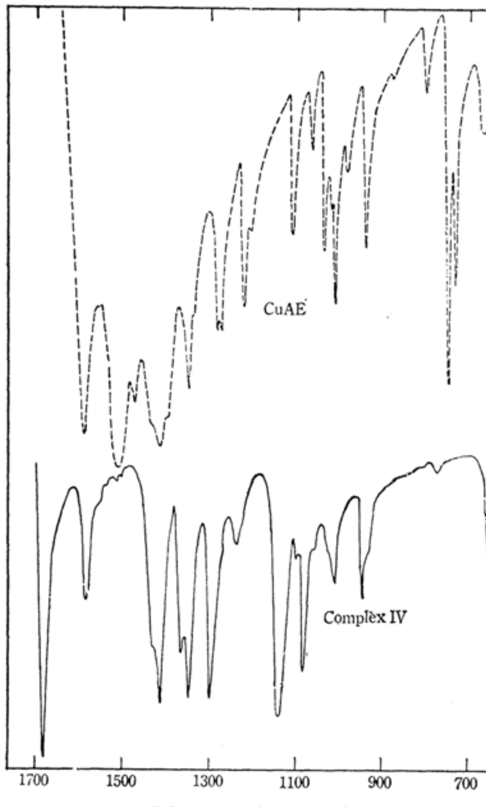

Fig. 7. IR spectra of CuAE and complex IV.

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7) J. P. Collman, R. L. Marshall, W. L. Young and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962); H. F. Holtzclaw and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).

8) M. Tamaki, Y. Nigo, I. Masuda and K. Shinra, Presented at the 21th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[*3] Tris(isonitrosoacetylacetonato)Co(III) is abbreviated Co(INA)$_3$.

9) C. Matsumoto and K. Shinra, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **88**, 340 (1967).

for a band at 1520 cm^{-1}. This band can be assigned to the stretching frequency of C=O that is coordinated to the cobalt atom; the corresponding bands are not observed for complexes II, IV and V (Figs. 6—8). The stretching frequency of non-coordianted C=O to the metal in Co(IAN)$_3$ appeared at 1660 cm^{-1}.

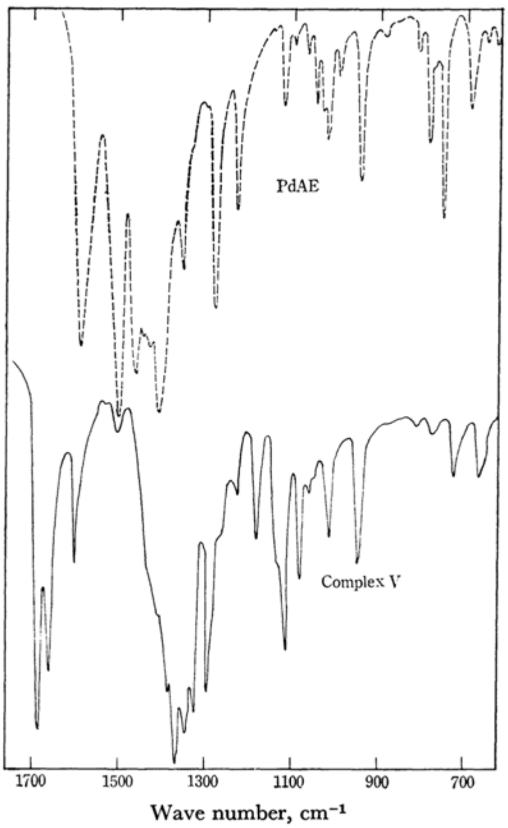

Fig. 8. IR spectra of PdAE and complex V.

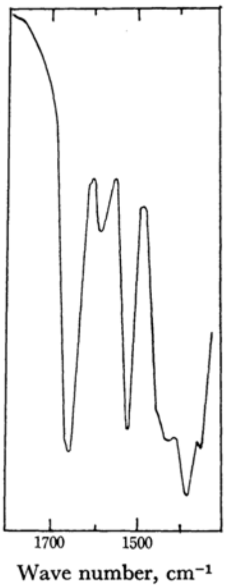

Fig. 9. IR spectra of Co(INA)$_3$.

On the basis of the spectrum of Co(INA)$_3$, the spectra of complexes II, IV and V may be reasonably explained by proposing the structures shown in Fig. 3. Assignments are listed in Table 2. The band at 1682—1689 cm^{-1} has been assinged to the stretching frequency of C=O that is not bound to the central metal atom. As for the subsidiary peak at a lower wave number (1660—1662), it is discussed later and is ascribed to the freqnency of the imine type C=N stretching in the porposed structure (Fig. 3).

Complex I shows interesting spectral features in that it possesses essentially the same frequencies of both complex II and the original NiAE. For example, as shown in Fig. 10 and Table 2, it exhibits bands at 1685 and 1652 cm^{-1}, corresponding to

TABLE 2. CHARACTERISTIC IR ABSORPTIONS OF THE COMPLEXES

Complex	Predominant modes					
	C=O str.	C=N str.[a)]			C=O str.[b)]	π_{C-H}
NiAE*2				1598 s	1522 s	765 m, 755 m
I	1685 s	1652 s		1605 s	1520 s	778 m
II	1689 vs	1660 m	1568 w			
CuAE				1588 s	1510 s	745 s, 730 m
III	1679 s			1598 s	1510 s	762 m
IV	1682 s		1587 m			
PdAE				1596 s	1502 s	758 m
V	1683 s	1662 s	1600 m			
Co(INA)$_3$*3	1660 s		1590 w		1520 s	

a) imine type C=N in chelate, b) C=O in chelate.

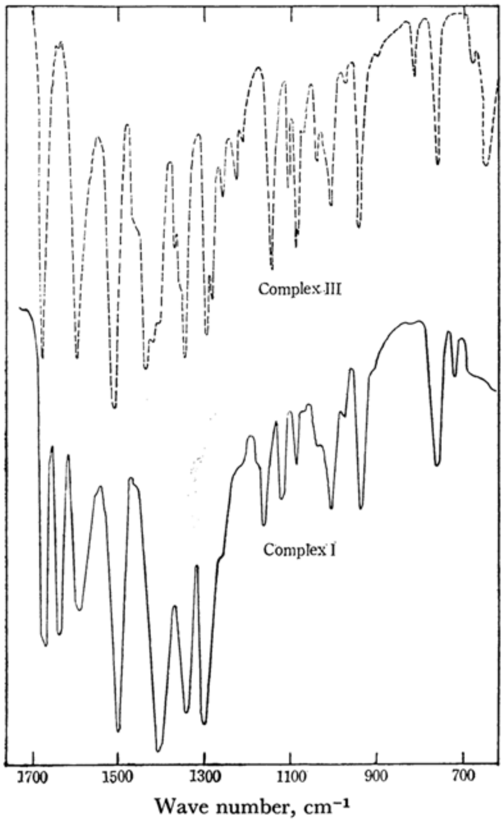

Fig. 10. IR spectra of complex I and complex III.

those at 1689 and 1660 cm^{-1} for complex II, and frequencies at 1605 and 1520 cm^{-1} corresponding to those at 1598 and 1522 cm^{-1} for NiAE. This peculiar feature of the spectrum is found over the 1700—300 cm^{-1} region (Figs. 10 and 11). In addition, complex I still shows the π_{C-H} band at 778 cm^{-1}. Cu complex III also has a rather similar spectrum to complex I (Figs. 10 and 12), indicating similar structures.

This fact may make one suspect complex I to be a mixed crystal of NiAE and complex II. However, from a chloroform solution of NiAE and complex II in a 1 : 1 molar ratio, a red crystal of complex I was not successfully crystallized. Complex I is shown to be monomeric in toluene by a molecular weight measurement. Thus, without presuming a structure such as shown in Fig. 2, the spectral features of complex I, described above, could hardly be understood.

Presuming this structure (Fig. 2), the bands at 1685 and 1520 cm^{-1} for complex I can be assigned to the stretching vibrations of the non-coordinated and coordinated C=O groups, respectively. The band at 1652 cm^{-1} is likely to be due to the stretching vibration of the imine type C=N groups in the complex (Fig. 2).

A chloroform solution of complex I has two peaks at 1685 and 1652 cm^{-1}, as in KBr. These two peaks do not change in intensity ratio with concentration of the complex. This fact indicates that the band at 1652 cm^{-1} can not be attributed to the associated C=O group, although the association of C=O is known to gives rise to a subsidiary peak at a lower wave number than the main peak of the unassociated C=O, as is seen in the case of a 1,2-diketonemonoxime such as diacetylmonoxime.10) The value, 1652 cm^{-1}, is thought to be considerably higher than that of the C=N stretching frequency of the oxime group in a complex. Usually the frequency of the oxime type C=N stretching in a conjugate system is observed10) at about 1630 cm^{-1}, and it can be expected to absorb below 1600 cm^{-1} in an unsaturated metal chelate such as shown in Fig. 2, judging from infrared evidence on metal - dimethylglyoximato complexes.11) The band at 1652 cm^{-1} for complex

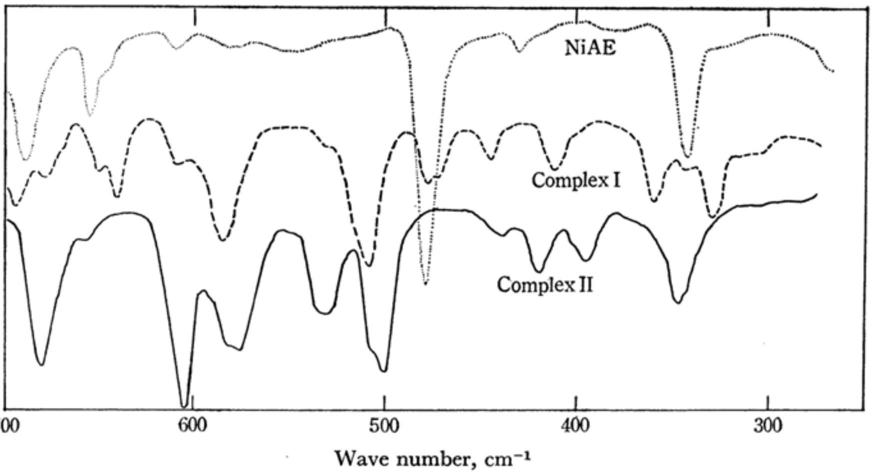

Fig. 11. IR spectra of NiAE, complex I and complex II.

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10) M. Kimura, Y. Kuroda and H. Takagi, This Bulletin, **33**, 1086 (1960).

11) K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).

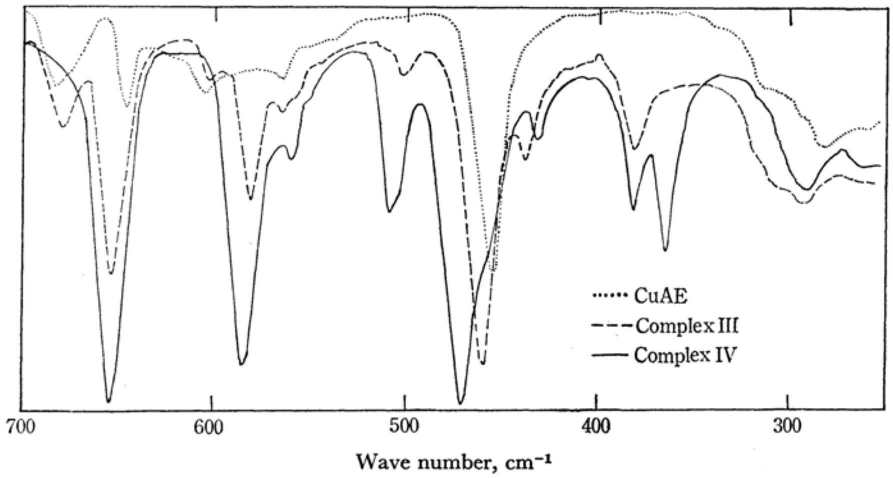

Fig. 12. IR spectra of CuAE, complex III and complex IV.

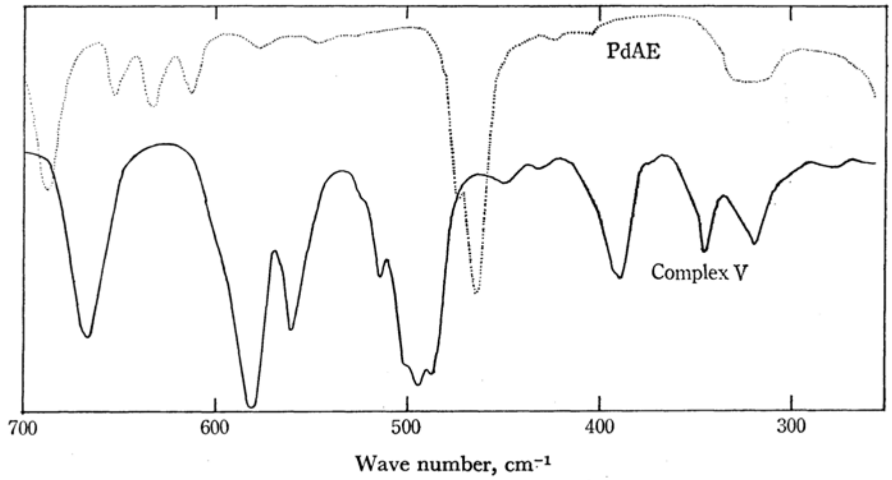

Fig. 13. IR spectra of PdAE and complex V.

I has therefore been ascribed to the stretching of the imine type C=N in the five-membered metal-chelate ring (Fig. 2).

In the spectra of Cu complexes III and IV (Figs. 7 and 10, and Table 2), the band due to the imine type C=N is not observed in the corresponding wave number region. In these cases, the absorption of C=O probably obscures the C=N absorption, whose frequency would be shifted toward higher wave numbers than for the other complexes.