BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2858—2862 (1969)

# Nitrosyl Complexes of Bis(acetylacetone)-, and Bis(benzoylacetone)-ethylenediimine Cobalt(II)

Motonori Tamaki, Isao Masuda and Koichiro Shinra

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

(Received March 27, 1969)

Square, planar bis(acetylacetone)-, and bis(benzoylacetone)-etylenediimine-Co(II) chelates with a low-spin d$^7$ electron structure yield nitrosyl complexes with the chelate : NO molar ratio of 1 : 1. On the basis of the IR spectra and the NMR spectra, and on the basis of molecular-weight determinations, these nitrosyls have been considered as being penta-coordinate cobalt complexes with square-pyramidal configuration. The nitrosyls are diamagnetic, indicating an electron-pairing bond between the central Co(II) and the NO molecule. The NO groups in these nitrosyls have been postulated to be predominantly neutral. In the electronic spectra, these penta-coordinate, diamagnetic Co(II) complexes show a characteristic absorption band at 18—$20\times10^3$ cm$^{-1}$ with $\log \varepsilon \doteqdot 3$.

The transition metal complexes of the bis(acetylacetone)-ethylenediimine Schiff base are considered to undergo two types of reaction with nitric oxide: i) at $\gamma$-carbon atoms in the chelate rings, and ii) at the central metal atom. The nickel(II) and palladium(II) complexes, in which the central metal ion has a spin-paired, d$^7$ electron structure, have already been shown to react with nitric oxide to produce oxime-type complexes such as are shown in Fig. 1.[1] This type of complex may be regarded as a product of i reaction.

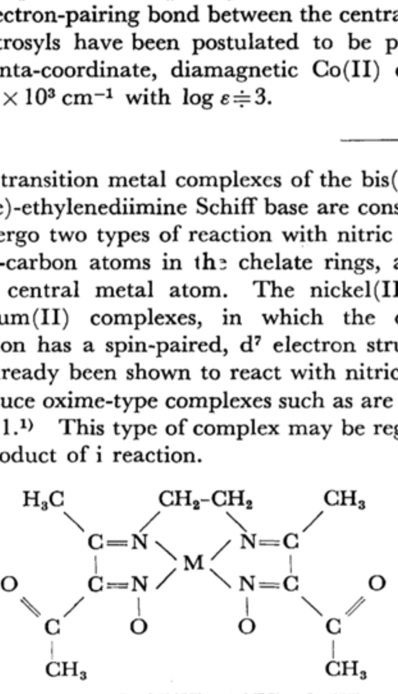

Fig. 1. M=Ni(II), Pd(II), Cu(II)

In the present work, divalent, low-spin cobalt(II) complexes with one unpaired electron will be shown to react with nitric oxide to form nitrosyl complexes, which are regarded as products of the ii reaction. These nitrosyl complexes are diamagnetic, and they are supposed to be penta-coordinate, square-pyramidal Co(II) complexes (Fig. 4) where the Co-NO bonding is essentially a $\sigma$-bond formed by one unpaired electron of NO and one of Co(II).

A copper(II) chelate with bis(acetylacetone)-ethylenediimine possessing one unpaired electron on the central metal ion yields either nitrosyl- or oxime-type complexes, depending on the experimental conditions.[1,2]

## Experimental

**Materials.** *The bis(acetylacetone)ethylenediimine,* AEH$_2$ *and bis(benzoylacetone)ethylenediimine,* BEH$_2$[*1] were prepared according to the method of the literatures.[3,4] AEH$_2$; recrystallized from water, mp 110—110.7°C. BEH$_2$; recrystallized from ethanol, mp 179.5—180.5°C.

*Bis(acetylacetone)ethylenediimino-Co(II),*[3] CoAE; purified by recrystallization from hot ether and then dried at 100°C *in vacuo* over P$_2$O$_5$; reddish yellow crystals.

*Bis(benzoylacetone)ethylenediimino-Co(II),*[4] CoBE; recrystallized from an acetone or benzene solution, and dried *in vacuo* over P$_2$O$_5$, at room temperature.

*The nitric oxide* was generated and purified by the method reported previously.[1]

**Preparations of Nitrosyl Complexes.** *Bis(acetylacetone)ethylenediimino-nitrosyl-cobalt(II),* Co$^{II}$AENO.[*1]. The complex can be prepared by the following three methods:

*A)* 2.8 g (0.01 mol) of CoAE were dissolved in 50 *ml* of dichloromethane. Nitric oxide was bubbled through this solution with ice cooling for about half an hour, by which time the solution had turned from reddish yellow to brown. Then, the nitric oxide in the solution was expelled with nitrogen gas. The addition of 250 *ml* of petroleum ether to the solution gave a precipitate of brownish-black compounds, which were then purified by recrystallization from a large volume of ether to give black crystals (complex I). The complex I is insoluble in water, and soluble in such

---

[1] I. Masuda, M. Tamaki and K. Shinra, This Bulletin, **42**, 157 (1969).

[2] M. Tamaki, Y. Nigo, I. Masuda and K. Shinra, presented at the 21th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[*1] AEH$_2$ and BEH$_2$ represent bis(acetylacetone)-ethylenediimine and bis(benzoylacetone)ethylenediimine, respectively.

[3] G. Morgan and J. Smith, *J. Chem. Soc.*, **1925**, 2030.

[4] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).

TABLE 1. ELEMENTARY ANALYSES OF THE COMPLEXES

| Complex | | Calcd % | | | | Found % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Co | C | H | N | Co | C | H | N |
| I* | $CoC_{12}H_{18}N_3O_3$ | 18.97 | 46.30 | 5.78 | 13.50 | 19.14 | 46.29 | 5.99 | 13.46 |
| I** | $CoC_{12}H_{18}N_3O_3$ | 18.97 | 46.30 | 5.78 | 13.50 | | 45.27 | 5.62 | 13.68 |
| II | $CoC_{22}H_{22}N_3O_3$ | 13.53 | 60.69 | 5.10 | 9.65 | 13.47 | 60.43 | 4.95 | 9.62 |

* Prepared by method A

** Prepared by method C

common organic solvents as ether, chloroform, dimethylformamide, and dimethyl sulfoxide. The results of the elementary analysis given in Table 1 correspond to that of the formula shown in Fig. 4.

*B)* CoAE, in the solid state, absorbs nitric oxide and yields the nitrosyl complex. Crystalline CoAE was allowed to stand in a nitric oxide atmosphere under a pressure of 760 mmHg, and at room temperature. The CoAE thereupon took up the nitric oxide and turned brownish-black. The recrystallization of this product from ether gave black crystals. Elementary analyses and a study of the IR spectrum indicated that the black compound obtained was identical with the complex I prepared by the method A.

*C)* The complex I was most expeditiously prepared by the following procedure. 2.5 g (0.01 mol) of cobaltaous acetate tetrahydrate were dissolved in 50 m*l* of methanol, and the air was expelled from the solution and reaction flask by flushing with nitrogen. Then the solution, with ice cooling, was saturated with nitric oxide until it had turned from a reddish violet to a dark violet. Then $AEH_2$ (2.3 g, 0.01 mol) dissolved in 50 m*l* of acetone was stirred into this dark-violet solution, drop by drop. The solution thereupon turned black. The nitric oxide in the solution was then driven off by nitrogen. The addition of petroleum ether to the solution gave a black precipitate of the crystalline, nitrosyl complex. The complex was proved by elementary analyses and by a study of the IR spectral data to be identical with the complex I.

*Bis(benzoylacetone)ethylenediimino-nitrosyl-cobalt(II)*, Co$^{II}$-BENO.[*1] This complex was prepared according to the method C. In this case, however, because of the poor solubility of $BEH_2$, 3.5 g (0.01 mol) of it were suspended in 50 m*l* of acetone; then the mixture was saturated with nitric oxide, followed by the addition of 2.5 g (0.01 mol) of cobaltous acetate tetrahydrate in 50 m*l* of methanol. The black precipitate was recrystallized from acetone to give 2 g of black needles (complex II). The elementary analyses agreed with the formula shown in Fig. 4. The complex II is insoluble in water and soluble in common organic solvents, but it is, unlike the complex I, insoluble in ether.

*Bis(salicylaldehyde) enthylenediimino - nitrosyl - cobalt(II)*, Co$^{II}$(Salen)NO.[*2] This complex has already been presented by Earnshaw *et al.*[5] In the present study it was prepared according to the method C. The complex obtained showed, in its IR spectrum, the same characteristic frequencies as those reported by Earnshaw,[5] and the analysis of the complex agreed with the structure written above.

## Measurements and Results

Molecular weight was determined in chloroform solution at 25°C, with a Mechrolab vapor pressure osmometer 302. The results are listed in Table 2.

The magnetic measurements were carried out at room temperature by the Gouy method, using an aqueous nickel(II) chloride solution as the standard. The magnetic susceptibilities obtained at 20°C for solid samples were; $-0.42\times10^{-6}$ emu/g for the complex I, and $-0.39\times10^{-6}$ emu/g for the complex II. These values indicate that the complexes are diamagnetic.

TABLE 2. MOLECULAR WEIGHT IN $CHCl_3$

| | Calcd* | Found |
|---|---|---|
| Complex I | 311 | 303 |
| Complex II | 435 | 429 |

* Calculated on the basis of the formula shown in Fig. 4.

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were carried out by using a Rigakudenki thermobalance at a heating rate of about 2°C/min. The curves thus obtained are shown in Figs. 2 and 3. In the TGA curve of the complex I, the weight loss of

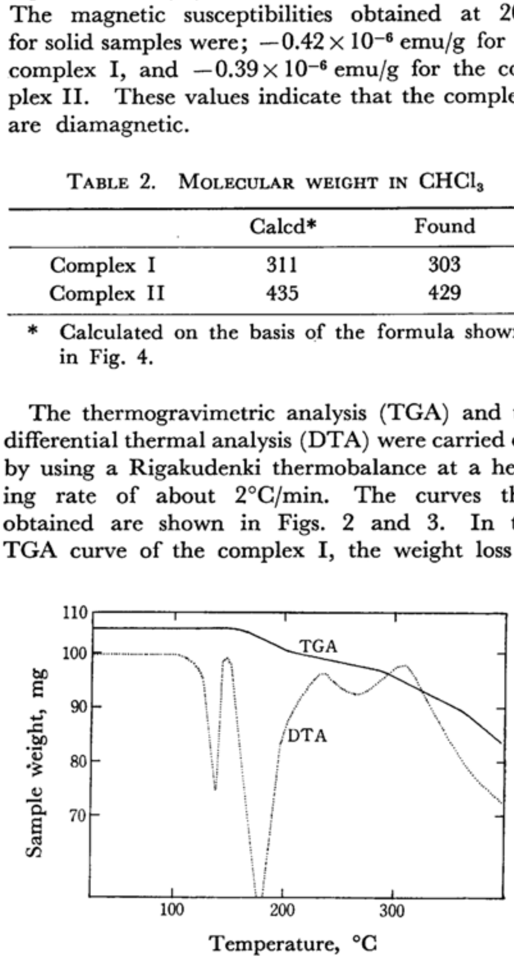

Fig. 2. DTA and TGA curves of complex I.

---

[*2] $SalenH_2$ represents bis(salicylaldehyde)ethylenediimine.

5) A. Earnshaw, P. C. Hewlett and L. F. Larkworthy, *J. Chem. Soc.*, **1965**, 4718.

about 9% observed between 160°C—200°C corresponds to the calculated value of 9.7%; the weight loss is assumed to be caused by the loss of the nitric oxide in the complex (Fig. 4). In the case of the complex II, no weight loss was observed below 200°C, as is shown in Fig. 3, indicating that the complex II is more stable than the complex I.

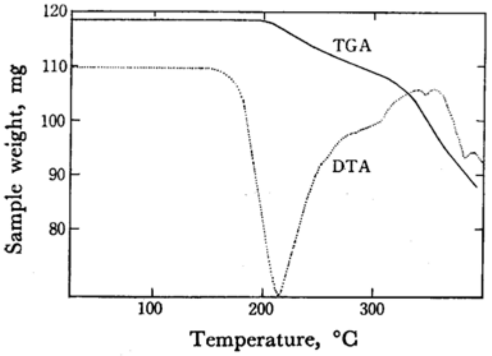

Fig. 3. DTA and TGA curves of complex II.

The NMR spectra were obtained with a Japan Electron Optics JNM-3H-60 spectrometer, at 60 Mc/sec, using tetramethylsilan (TMS) as the internal reference. The NMR spectrum of complex I in a 5 wt% $CDCl_3$ solution is, in Fig. 5, compared to the spectrum of the NiAE complex.

The IR spectra were measured in Nujol or in hexachlorobutadiene, using a Hitachi EPI-2G spectrometer for the 4000—650 cm$^{-1}$ region. The IR spectra obtained for the complex I and II are shown in Figs. 6 and 7. The electronic absorption spectra of the complexes I and II, which were determined in chloroform using a Hitachi EPS-3 spectrophotometer, are shown in Fig. 8.

## Discussion

The elementary analyses for the complexes I and II agreed well with those of the mono-nitrosyl derivatives of CoAE and CoBE respectively, as is shown in Fig. 4. The molecular weight, determined in chloroform, is consistent with this formula:

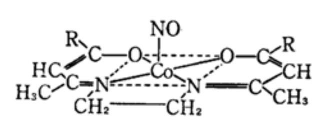

Fig. 4. Complex I: R=$CH_3$
Complex II: R=$C_6H_5$

**NMR and IR Spectra.** The above formulation of the complexes was examined further by the following considerations of the NMR and IR spectral evidence. As may be seen in Fig. 5, the NMR spectra of the complex I in $CDCl_3$ shows four peaks, at τ; 5.1, 6.5, 7.8, and 7.95, with an integral ratio of 1 : 2 : 3 : 3 from the lower-side field. The features of this spectrum are quite similar to those of NiAE or $[CoAE(NH_3)_2]Cl$;⁽⁶⁾ the above four resonances may, therefore, be assigned to the CH group, to the $CH_2CH_2$ group, and to two types of $CH_3$ groups of the complex (Fig. 4, R=$CH_3$) respectively.

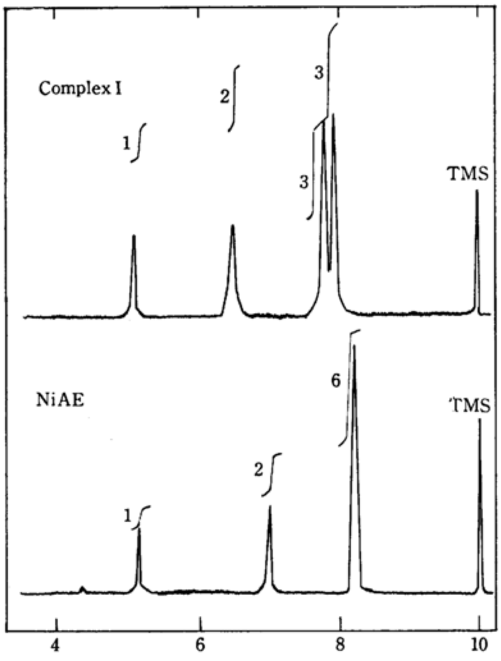

Fig. 5. NMR spectra of complex I and NiAE.

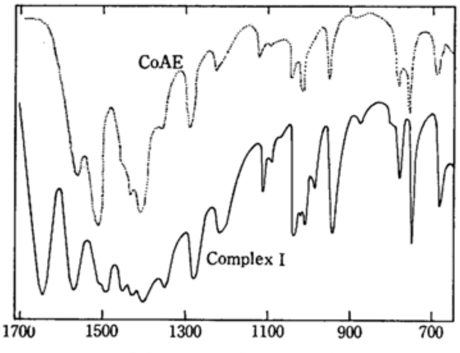

Fig. 6. IR spectra of complex I and CoAE.

A comparison of the IR spectrum of the complex I in the 1700—700 cm$^{-1}$ range with that of the CoAE indicates that, as is shown in Fig. 6, the complex I has essentially the same pattern of frequencies as the CoAE, with the exception of a

---

6) H. Yoneda and Y. Morimoto, This Bulletin **41**, 2544 (1968); P. J. McCarthy and A. E. Martell, *Inorg. Chem.*, **6**, 781 (1967).

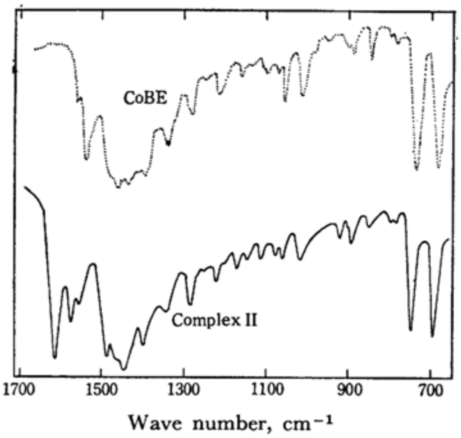

Fig. 7. IR spectra of complex II and CoBE.

new frequency at 1654 cm$^{-1}$. Similarly, the complex II shows the same frequencies as those of the CoBE except for a new frequency at 1635 cm$^{-1}$, as may be seen in Fig. 7. The new frequencies will be discussed later as being due to the nitric oxide group in the complexes (Fig. 4).

Thus, from the above-described NMR and IR spectral evidences and from the analytical results, we may assume such a nitrosyl structure for the two complexes, I and II, as is shown in Fig. 4, where the cobalt atom in the planar chelate is bound to a nitric oxide group to form a penta-coordinate, square pyramidal configuration. The nitrosyl complexes are monomeric in chloroform and contain, in the solid state, no solvent, as is indicated by the TGA curves (Figs. 2 and 3).

Most of the nitrosyl complexes have so far been characterized by a strong, nitrosyl-stretching frequency. Lewis *et al.*[7] have surveyed numerous nitrosyl complexes of transition metals on the basis of the nitrosyl frequencies in the IR spectra. In general, the position of the nitrosyl frequency is susceptible to the electronic structure of the nitrosyl group in the complex and to the nature of the central metal ion. For example, the NO frquency is observed at 1626 cm$^{-1}$ for $\{(CH_3)_2NCS_2\}_2CoNO$, at 1673 cm$^{-1}$ for $\{(C_2H_5)_2NCS_2\}_2FeNO$, and at 1845 cm$^{-1}$ for $\{(CH_3)_2NCS_2\}_3RuNO$.[7] Hecne, it would be more appropriate to take into account analogous nitrosyl complexes containing the same metal ion when the nitrosyl frequency is taken as an indication of the structure of the complex. Table 3 lists the cobalt-nitrosyl complexes, along with the positions of their NO stretching frequencies. As can be seen in this table, most of these nitrosyl complexes, which are apparently penta-coordinate and diamagnetic, show the characteristic NO frequency in the 1623—1705 cm$^{-1}$ range. As has been described before, the complexes I and II, which are penta-coordinate and diamagnetic, show new absorption bands at 1654 and 1635 cm$^{-1}$ respectively. These new bands can reasonably be assigned to the NO stretching frequency on the basis of the facts presented in Table 3.

Lewis *et al.*[7] postulated two types of NO groups existing in complexes; the $(NO)^-$ anion which shows a $(NO)^-$ stretching frequency at around 1200 cm$^{-1}$, exemplified by $[Co(8\text{-aminoquinoline})_2NO]Cl_2$ (Table 3), and the $(NO)^+$ cation which is said to show a characteristic frequency over the

Table 3. IR characteristic frequencies and magnetic properties of nitrosyl complexes

| Nitrosyl complex | NO str., cm$^{-1}$ | Mag. property*** | Ref. |
|---|---|---|---|
| Co{bis(acetylacetone)ethylenediimine}NO* | 1654 | d.m | present work |
| Co{bis(benzoylacetone)ethylenediimine}NO** | 1635 | d.m | present work |
| Co(acetylacetonate)$_2$NO | 1675 | d.m | 8 |
| Co{bis(salicylaldehyde)ethylenediimine}NO | 1624 | d.m | 5 |
| Co(*N,N'*-diethyldiselenocarbamate)$_2$NO | 1623 | | 9 |
| Co(*N,N'*-dimethyldithiocarbamate)$_2$NO | 1626 | d.m | 10, 11 |
| Co(phthalocyanine)NO | 1705 | | 12 |
| [Co(ethylenediamine)$_2$NO](NO$_3$)$_2$ | 1645 | d.m | 13 |
| [Co(8-aminoquinoline)$_2$NO]Cl$_2$ | 1170 | 3.45 B.M | 14 |
| Na$_2$[Co(NO$_2$)$_4$(OH)NO] | 1740 | | 7 |

* complex I  ** complex II  *** d.m, diamagnetic; B.M, Bohr Magneton

---

[7] J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958); W. P. Griffith, J. Lewis and G. Wilkinson, *ibid.*, **7**, 38 (1958).

[8] R. Nast and H. Bier, *Chem. Ber.*, **92**, 1958 (1959).

[9] K. A. Jensen and V. Karishnan, *Acta Chem. Scand.*, **21**, 2904 (1967).

[10] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

[11] R. L. Carlin, F. Canziani and W. K. Bratton, *J. Inorg. Nucl. Chem.*, **26**, 898 (1964).

[12] C. Ercolani, C. Neri and G. Sartori, *J. Chem. Soc.*, **A 1968**, 2123.

[13] T. B. Jackson, M. J. Baker, J. O. Edwards and D. Tutas, *Inorg. Chem.*, **5**, 2046 (1966).

[14] R. Nast, H. Bier and J. Gremm, *Chem. Ber.*, **94**, 1185 (1961).

wide range from 1626 to 1938 cm$^{-1}$.7) Accepting their point of view, the complexes I and II should contain $(NO)^+$ and, consequently, Co(I). However, the complexes are actually more stable than Co(I) complexes might be expected to be. The polarographic behavior[*3] indicated that these complexes contained neutral NO and Co(II). Thus, it seems more probable to ascribe the new bands observed at 1654 or 1635 cm$^{-1}$ in the present complexes to the stretching frequency of predominantly neutral NO. The NO molecule shows the stretching frequency at 1878 cm$^{-1}$,15) and one would expect a shift towards the lower-wave number region upon complexation. On the other hand, the nitrosonium ion $(NO)^+$ is known to show the frequency at $\sim$2220 cm$^{-1}$.16) Therefore, in the case of the nitrosyl complexes that shown the NO frequency in the wave number region higher than 1878 cm$^{-1}$, the NO group may be regarded as being $(NO)^+$, as is seen in $[Fe^{II}(CN)_5(NO)]^{2+}$ (1938 cm$^{-1}$).7) As far as cobalt-nitrosyls are concerned, there are but a few examples which show NO frequencies in a wave number region higher than 1800 cm$^{-1}$.7)

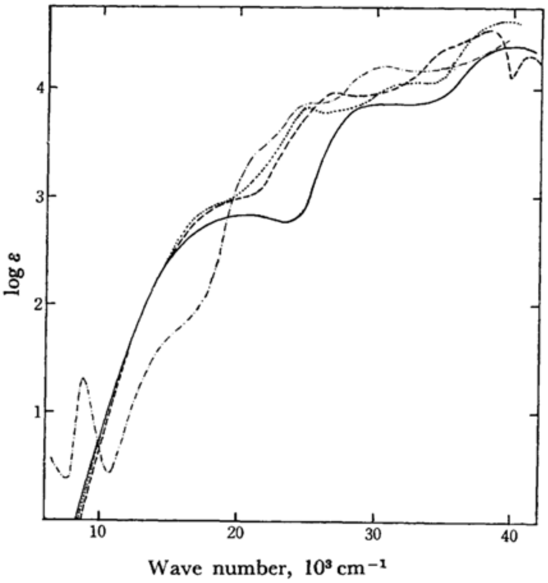

Fig. 8. Electronic spectra of complex I, complex II, Co(Salen)NO and CoBE.

—— Complex I ----- Complex II
........ Co(Salen)NO —·—· CoBE

**Electronic Spectra.** It has been well established that the electronic absorption spectra in the near-infrared region of Co(II) complexes are informative of the structure of the complexes. Nishikawa and Yamada17) established that the square-planar Co(II) complexes with one unpaired electron exhibit a sharp peak at about $8.3\times10^3$ cm$^{-1}$ ($\log\varepsilon\doteqdot1.3$). As may be expected from the above fact, the CoBE shows a sharp peak at $8.7\times10^3$ cm$^{-1}$ ($\log\varepsilon\doteqdot1.3$), as is shown in Fig. 8. On the contrary, a similar absorption band is not observed for either complex, I or II (Fig. 8), suggesting that the complexes have a symmetry different from that of the planar configuration of the parent complexes. This is consistent with the anticipation from the diamagnetic properties of the complexes I and II. As to the Co(Salen)NO[*2], an absorption band representative of square-planar, low spin Co$^{II}$(Salen)17) was not observed either. In the case of these nitrosyl complexes, an absorption band with $\log\varepsilon\doteqdot2.8$ appeared at 18—$20\times10^3$ cm$^{-1}$; this may be considered to be characteristic of the diamagnetic Co(II) complexes with square-pyramidal configuration. It is of interest to note that penta-coordinate alkyl derivatives of bis(acetylacetone)ethylenediimine cobalt complexes with a square-pyramidal configuration are reported to show absorption maxima at about $15\times10^3$ cm$^{-1}$ ($\log\varepsilon\doteqdot2.9$).18)

---

[*3] The polarogram of the CoBE in DMF gave a one-step reduction wave at −1.46 V (applied potential), whereas the complex II gave a two-step reduction wave, one step at −1.04 V which can be ascribed to the reduction of NO in the complex and one at −1.43 V that is almost equal to that (−1.46 V) of CoBE and which can be ascribed to the reduction of Co(II) in the complex. The details will be published later.

15) E. L. Saier and A. Pozefsky, *Anal. Chem.*, **26**, 1079 (1954).

16) D. J. Millen and D. Watson, *J. Chem. Soc.*, **1957**, 1369.

17) H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964).

18) G. Costa, G. Mestroni, G. Tauzher and L. Stefani, *J. Organometal. Chem.*, **6**, 181 (1966); G. Costa, G. Mestroni and L. Stefani, *ibid.*, **7**, 493 (1967).