1400 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1400—1403(1972) [Vol. 45, No. 5

The Nitration of Nickel(II)-, and Copper(II)-complexes of Bis(salicylaldehyde)ethylenediimine

Motonori TAMAKI, Isao MASUDA, and Koichiro SHINRA

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

(Received July 12, 1971)

The M(Salen) complexes (where $M=Ni^{II}$, Cu^{II}, Co^{II}-NO, and $V^{IV}O$, and where Salen=bis(salicylaldehyde)-ethylenediiminato dianion) were reacted with nitric oxide in organic solvents in the air. The free ligand can only form a compound with the formula of $SalenH_2 \cdot 2HNO_3$, while the complexes with M=Ni or Cu gave NO_2-substituted complexes, M(5,5′-dinitro-Salen), in almost quantitative yields. In the cases of Co(Salen)NO and VO-(Salen), no substitution reaction on the phenyl ring took place, but they formed a nitric acid adduct, $Co(Salen)NO \cdot nHNO_3 \cdot nH_2O$ ($n=1$ and 2) and $VO(Salen) \cdot HNO_3 \cdot H_2O$. The reactions are thought to proceed by means of a process involving a nitric acid. The reactivity of the Ni- and Cu-Salen complexes is explained in terms of a π-electron localization at the 5- and 5′-positions of the phenyl rings resulting from $d_\pi \rightarrow p_\pi$ back bonding. A lack of a similar substitution reaction in Co(NO)- and VO-Salen complexes is explained as being due to the lower stability in the metal-Salen bonding.

In previous studies of the reaction of the transition metal complexes with nitric oxide, it has been reported that Ni(II), Cu(II), and Pd(II) complexes of bis(acetylacetone)ethylenediimine, and Pd(II) complexes of acetylacetone and its derivatives react at the γ-position of the metal chelate rings to form α-imine-oxime-type complexes,[1,2] whereas in the case of Co(II) complexes of bis(acetylacetone)ethylenediimine and bis(benzoylacetone)ethylenediimine, a nitrosyl complex binding NO as an axial ligand is obtained.[3]

The present work will deal with the reaction of NO with Cu(II) and Ni(II) chelates, including bis(salicylaldehyde)ethylenediimine,[4] to produce NO_2-substituted complexes, M(5,5′-dinitro-Salen) (M=Ni and Cu).

Experimental

Materials. $SalenH_2$ and its metal complexes were prepared according to the method described in the references.

Reaction with Nitric Oxide. In the following experiments, NO was bubbled through the solution in air.

Ni(5,5′-dinitro-Salen)·1.5H₂O. A 1.5 g portion of Ni-(Salen)[5] was dissolved in 100 m*l* of acetonitrile. Bubbling NO through the solution at room temperature then resulted in the precipitation of an orange compound. After bubbling for two hours, the NO in the solution was driven off by N_2 gas; then the precipitates were collected by filtration. The compound was recrystallized from a large volume of acetonitrile to give fine crystals with an orange color (complex **1**). Complex **1** is soluble in acetonitrile and acetone. Yield, 1 g.

Found: C, 43.58; H, 3.21; N, 12.47%. Calcd for $NiC_{16}H_{15}N_4O_{7.5}$: C, 43.47; H, 3.43; N, 12.68%.

The complex **1** could also be obtained by a similar reaction in a chloroform solution. The greenish precipitates which separated were recrystallized from an acetonitrile solution to give orange crystals. The analytical and IR spectral data were consistent with those of the complex **1**.

Found: C, 43.85; H, 3.32; N, 12.41%. Calcd for $NiC_{16}H_{15}N_4O_{7.5}$: C, 43.47; H, 3.43; N, 12.68%.

Cu(5,5′-dinitro-Salen). One gram of Cu(Salen)[5] was dissolved in 150 m*l* of chloroform; when NO was then bubbled through this solution at room temperature for about three hours, brownish precipitates were separated. The NO in the solution was driven off by N_2 gas, and the precipitates were collected on a filter and washed with chloroform and then with ether. The precipitates were recrystallized from an anhydrous acetonitrile solution to give greenish-brown needles (complex **2**).

Found: C, 45.26; H, 2.87; N, 13.50%. Calcd for $CuC_{16}H_{12}N_4O_6$: C, 45.77; H, 2.86; N, 13.35%.

The same compound was also obtained by a reaction in an acetonitrile solution. The complex **2** including its water molecule, tends to crystallize when it is allowed to stand in a solution of an organic solvent in air; 2.5 hydrates are obtained from an acetonitrile solution, and 0.5 hydrates, from an acetone solution.

Co(Salen)NO·HNO₃·H₂O. One gram of Co(Salen)-NO[6] was dissolved in 150 m*l* of chloroform. NO gas was bubbled through this solution for five hours. The green complex thus precipitated was collected by filtration and was recrystallized from a mixed acetonitrile-ether solution as green crystals (complex **3**). Yield, 0.5 g.

Found: Co, 13.25; C, 44.41; H, 3.56; N, 13.02%. Calcd for $CoC_{16}H_{17}N_4O_7$: Co, 13.51; C, 44.04; H, 3.94; N, 12.84%.

Co(Salen)NO·2HNO₃·2H₂O. The reaction that was carried out in an acetonitrile solution resulted in the precipitation of a brownish-green compound. This was then recrystallized from a mixed acetonitrile-ether solution.

Found: Co, 11.50; C, 37.11; H, 3.45; N, 13.81%. Calcd for $CoC_{16}H_{20}N_5O_{11}$: Co, 11.39; C, 37.14; H, 3.90; N, 13.54%.

VO(Salen)·HNO₃·H₂O. A similar reaction of VO-(Salen)[7] in a chloroform solution gave dark violet precipitates, which were then recrystallized from methanol.

Found: C, 46.85; H, 3.96; N, 10.03%. Calcd for $VC_{16}H_{17}N_3O_7$: C, 46.39; H, 4.10; N, 10.15%.

SalenH₂·2HNO₃. Two grams of $SalenH_2$ were dissolved in 100 m*l* of chloroform; then NO was bubbled through the solution for about two hours. The white precipitates

---

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

[2] D. A. White, *J. Chem. Soc., A*, **1971**, 233.

[3] M. Tamaki, I. Masuda, and K. Shinra, This Bulletin, **42**, 2858 (1969).

[4] The following abbreviations are used in the present paper. Salen: bis(salicylaldehyde)ethylenediiminato dianion, 5,5′-dinitro-Salen: bis(5-nitro-salicylaldehyde)ethylenediiminato dianion, and 3,3′-dinitro-Salen: bis(3-nitro-salicylaldehyde)ethylenediiminato dianion.

[5] P. Pfeiffer, E. Breite, E. Lübbe, and T. Tsumaki, *Ann.*, **503**, 84 (1933).

[6] A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *J. Chem. Soc.*, **1965**, 4718.

[7] H. J. Bielig and E. Bayer, *Ann.*, **580**, 135 (1953).

which resulted were washed with chloroform. Yield, 1.5 g.

Found: C, 47.95; H, 4.49; N, 14.40%. Calcd for $C_{16}H_{16}N_4O_8$: C, 48.21; H, 4.21; N, 14.28%.

The addition of $NiCl_2 \cdot 6H_2O$ to an aqueous alkaline solution of $SalenH_2 \cdot 2HNO_3$ resulted in the precipitation of reddish-orange crystals, which were then recrystallized from chloroform. The elementary analytical and IR spectral data indicated the compound to be Ni(Salen).

Found: C, 58.86; H, 4.41; N, 8.55%. Calcd for $NiC_{16}H_{14}N_2O_2$: C, 59.12; H, 4.35; N, 8.62%.

The recrystallization of the $SalenH_2 \cdot 2HNO_3$ from methanol or ethanol gave thin plates whose analytical data correspond to those of (ethylenediamine)$2HNO_3$. This compound is thought to be a hydrolytic product of $SalenH_2 \cdot 2HNO_3$.

Found: C, 13.00; H, 5.37; N, 30.22%. Calcd for $C_2H_{10}N_4O_6$: C, 12.90; H, 5.43; N, 30.10%.

In an acetonitrile solution, $SalenH_2$ reacted with NO to produce (ethylenediamine)$2HNO_3$.

Measurements. The IR spectra were measured in Nujol or in hexachlorobutadiene, using a Hitachi 225 grating spectrometer for the 4000—200 cm^{-1} region and a JASCO IR-G spectrometer for the 4000—400 cm^{-1} region. The magnetic susceptibilities were determined at room temperature by the Gouy method. The electronic absorption spectra were obtained with a Hitachi EPS-3 spectrophotometer. The conductance measurements were made at 25°C using a Universal Bridge Model 4225A, Yokogawa Electric Works, Ltd.

Results and Discussion

Ni(Salen) and Cu(Salen) reacted with NO in the air, in chloroform or in acetonitrile, to form an orange-colored compound (complex **1**) or a greenish-brown compound (complex **2**) respectively. As will be discussed below, these compounds have been confirmed to be 5,5'-dinitro-substituted complexes.

In general, it would not be reasonable to expect a remarkable difference in the IR spectra between metal complexes with 5,5'- and with 3,3'-dinitro-Salen.[4] However, it can clearly be seen in the spectra (Fig. 1) of the Ni(II)-complexes with 5,5'- and 3,3'-dinitro-Salen prepared as authentic compounds[8] that: i) of the two bands at about 1600 cm^{-1}, the one at the higher wave number is more intense than the one at the lower wave number for the 5,5'-dinitro-complex, while the former is weaker than the latter for the 3,3'-dinitro-complex, and ii) the band about 1300 cm^{-1} is broader for the 5,5'-dinitro-complex. The IR spectrum of the complex **2** exhibits the characteristic feature of the 5,5'-dinitro-complex (Fig. 1). Thus, the complex **1** can be considered to be Ni^{II}(5,5'-dinitro-Salen)$\cdot 1.5H_2O$. Similarly, an inspection of the IR spectrum (Fig. 2) leads us to conclude that the complex **2** can be formulated as: Cu^{II}(5,5'-dinitro-Salen).[9,10]

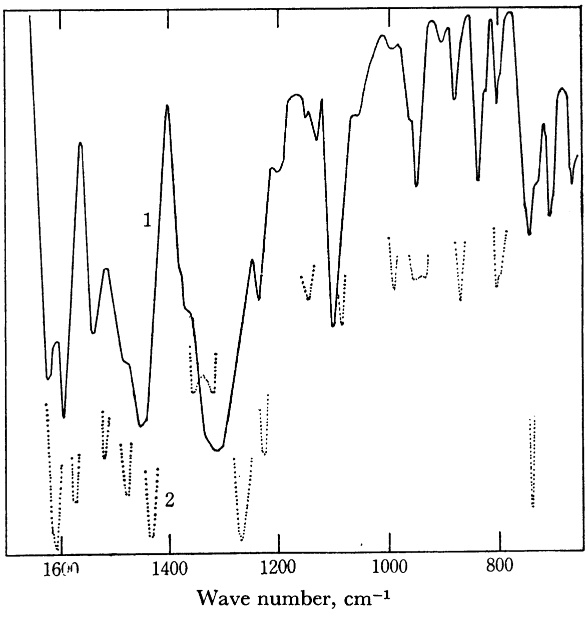


Fig. 1. IR spectra of Ni(5,5'-dinitro-Salen)$\cdot 1.5H_2O$[a]; ——, and Ni(3,3'-dinitro-Salen); ······, in Nujol.

a) The frequencies of the complex **1** is identical to the curve 1.

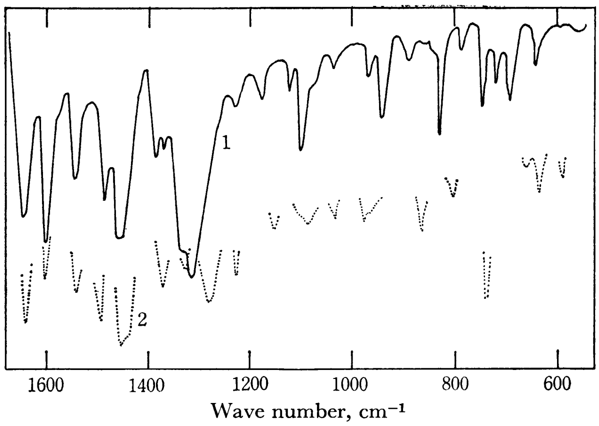


Fig. 2. IR spectra of Cu(5,5'-dinitro-Salen);[a] ——, and Cu(3,3'-dinitro-Salen); ······, in Nujol.

a) The frequencies of the complex **2** is identical to the curve 1.

The reaction of the free ligand ($SalenH_2$) with NO in a chloroform solution produced neither a nitroso- nor a nitro-substituted compound, but only formed the precipitates of a compound corresponding to the $SalenH_2 \cdot 2HNO_3$ formula. This was characterized as a nitric acid adduct of the Schiff base by reaction with the Ni^{2+} ion in an aqueous solution, thus forming Ni(Salen), and by recrystallization from methanol or ethanol, by which it was converted into (ethylenediamine)$2HNO_3$ in an almost quantitative yield.

As has been described above, the reactions resulted in the formation of the nitric acid adduct of the free ligand and the nitro-substituted metal-Salen complex. Moreover, the reactions can not be observed to occur with pure NO; that is solutions of $SalenH_2$ or its Ni- and Cu-complexes did not react with NO in the absence of air. Thus, the reactions may be thought to proceed by means of a process involving a nitric acid. Further, it is likely that the complex formation of $SalenH_2$ with the Ni^{2+} or Cu^{2+} ion makes it easy for the nitration reaction to take place at the 5- and 5'-positions of the phenyl rings. In the complexes, this can tentatively

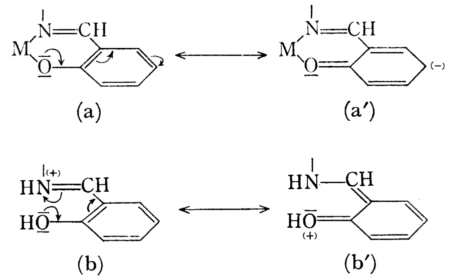
---

[8] E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem.*, **26**, 1577 (1964).

[9] C. S. Marvel and N. Tarköy, *J. Amer. Chem. Soc.*, **77**, 5820 (1955).

[10] T. Tanaka, *ibid.*, **80**, 4108 (1958); This Bulletin, **33**, 259 (1960).

be explained in terms of an electrophilic substitution reaction at the 5- and 5′-positions of the phenyl rings caused by a π-electron localization, as is shown in (a′).



(a) (a′)

(b) (b′)

It is probable that the coordination bond between the nitrogen atom and the metal ion can participate in the mesomeric system through the $d_\pi \rightarrow p_\pi$ back donation, thus increasing π-localization on the 5- and 5′-positions.

On the other hand, the free $SalenH_2$ tends to form a proton-addition compound which may act to decrease the degree of π-localization on the 5- and 5′-carbons, as is shown in (b′).[11]

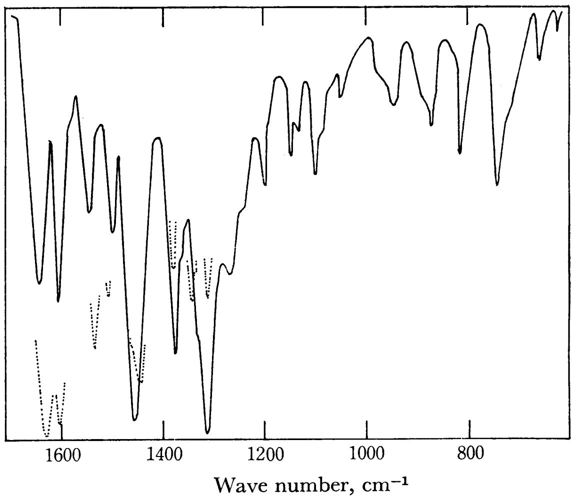


Fig. 3. IR spectra of $Co(Salen)NO \cdot HNO_3 \cdot H_2O$;——, and Co(Salen)NO;······, in Nujol.

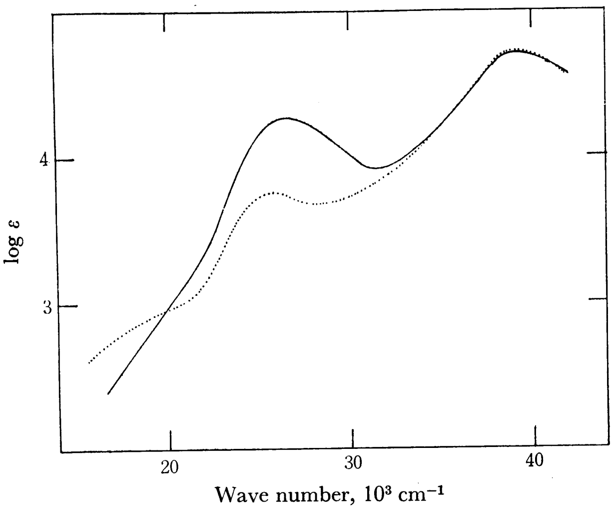


Fig. 4. Electronic spectra of $Co(Salen)NO \cdot HNO_3 \cdot H_2O$;——, and Co(Salen)NO;······, in acetonitrile.

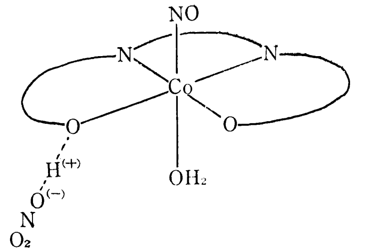


Fig. 5.

It should be noted that, in the case of the Co(Salen)-NO, no similar substitution reaction could be observed. It has already been reported that, by reaction with NO in organic solvents, Co(Salen) easily produces Co(Salen)-NO,[6] wherein the Salen is coordinated to the cobalt ion in the plane, as in the cases of Ni(II)- and Cu(II)-Salen. Hence, it seems possible to expect a similar nitration reaction to take place in the case of Co(Salen)NO. However, in fact, Co(Salen)NO afforded only a diamagnetic compound (complex **3**) which can be formulated as a nitric acid adduct, $Co(Salen)NO \cdot HNO_3 \cdot H_2O$. The IR spectrum of this adduct (Fig. 3) obviously differs from that of the Co(II) complexes with 5,5′- and 3,3′-dinitro-$SalenH_2$,[6] and possesses the characteristic absorptions for the NO group at 1640 cm^{-1} and for the NO_3^- group (ν_3) at about 1300 cm^{-1}.[12] The electronic absorption spectrum of this compound (Fig. 4) shows a maximum at 39.1×10^3 cm^{-1} which quite resembles Co(Salen)NO. On the other hand, in the 18—20×10^3 cm^{-1} region its spectrum differs remarkably from that of Co(Salen)NO and does not show the characteristic peak of penta-coordinate, diamagnetic Co(II) complexes.[3] Judging from these observations and the analytical data, a skeletal structure for this adduct is tentatively drawn in Fig. 5. When reacted in an acetonitrile solution, Co(Salen)NO binds two moles of HNO_3. In the case of VO(Salen), $VO(Salen) \cdot HNO_3 \cdot H_2O$ was separated by a similar reaction in a chloroform solution. The conductance data shown in Table 1 seem to be consistent with the formula of the adduct of the VO-complex. The adduct of the Co-complex shows less conductivity than would be expected for a 1 : 1 electrolyte.

The lack of a similar substitution reaction for Co-(Salen)NO may be explained as follows. There seem to be no numerical data available for discussing the relative stabilities of a series of the metal-Salen com-

TABLE 1. ELECTRIC CONDUCTANCE; IN ACETONITRILE

	Concn. (M)	Molar conductance ($cm^2/\Omega \cdot mol$)
$Co(Salen)NO \cdot HNO_3 \cdot H_2O$ (complex **3**)	1/250	2.43
$VO(Salen) \cdot HNO \cdot H_2O$	1/500	45.1
VO(Salen)	1/250	0.270
$[Co(dmgH)_2(py)_2]Cl$[a]	1/250	60.5

a) dmgH and py represent dimethylglyoximato monoanion and pyridine, respectively.

---

[11] The adducts of Cu(Salen) with phenol and propionic acid are prepared by Tanaka, in Ref. 10.

[12] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination compounds," John Wiley, & Sons, New York and London (1962), p.90.

plexes. However, judging from the common order of the stability constants,[13] Ni(II)- and Cu(II)-complexes may be expected to be the most stable of the Salen complexes used in the present work. When the bond of Co–N is more unstable, the degree of the $d_\pi \rightarrow p_\pi$ back donation is assumed to be more decreased in the metal complexes other than Ni and Cu. In the cases of the Co(NO)- and VO-complexes, the further formation of the bonding with the axial ligand may also cause a weakening of the bonding between metal and Salen.[14]

---

[13] D. P. Mellor and L. Malay, *Nature*, **159**, 370; H. Irving *Proc. Intern. Conf. on Coordination Chem.*, Chem. Soc. London, (1959), p. 13.

[14] T. Shigematsu, M. Tabushi, M. Matsui, and M. Munakata, This Bulletin, **41**, 2656 (1968).