January, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 171—174(1972) 171

The Preparation of Bis(dimethylglyoximato)nitrosylcobalt(II) and its Conversion into the Nitro Complex

Motonori TAMAKI, Isao MASUDA, and Koichiro SHINRA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita

(Received June 21, 1971)

The preparation of diamagnetic $Co^{II}(dmgH)_2NO$ (dmgH=dimethylglyoximato monoanion) is reported. The complex shows the IR absorption band of NO at 1641 cm^{-1}, indicating a neutral NO ligand in the complex. The IR and electronic spectra are consistent with the structure of the penta-coordinate, the square-pyramidal configuration of the complex. In the presence of oxygen and water, the complex is oxidized rapidly ($NO \rightarrow NO_2^-$, $Co(II) \rightarrow Co(III)$) and converted into $Co^{III}(dmgH)_2NO_2 \cdot OH_2$. During the reaction, a complex formulated as $[Co^{II}(dmgH)_2NO \cdot OH_2][Co^{III}(dmgH)_2NO_2] \cdot 2H_2O$ is obtained. It is considered that, in the complex, the Co(II) is bound with the Co(III) through a NO bridge. The assignments of the IR spectra have been made using ^{15}NO and $^{15}NO_2$.

Thus far, many transition metal nitrosyl complexes have been prepared.[1] The low-spin Co(II) complexes with square-planar configurations are known to bind NO, thus forming diamagnetic, penta-coordinate Co(II) complexes with square-pyramidal configurations, such as CoAE(NO), CoSalen(NO), and $Co(dtc)_2(NO)$.[2,3] Recently, Schrauzer and Windgassen isolated planar $Co(dmgH)_2$,[2,4] with a magnetic moment of 1.70 B.M.

In this paper, the preparation and properties of $Co^{II}(dmgH)_2NO$ will be described. Of the transition-metal nitrosyl complexes with the same type of structure, the present complex is anomalous in that it is oxidized easily to form the nitro-Co(III) complex, $Co^{III}(dmgH)_2NO_2 \cdot OH_2$.

Experimental

Preparation of the Complexes. Bis(dimethylglyoximato)nitrosylcobalt(II), $Co^{II}(dmgH)_2NO$*; Complex I:* a) $Co(CH_3COO)_2 \cdot 4H_2O$ (2.5 g) was dissolved in 30 m*l* of methanol, and the solution was saturated with NO at 0°C. Into this solution we stirred, drop by drop, dimethylglyoxime (2.3 g) suspended in 60 m*l* of ethanol. Bubbling NO into the solution for about 2 hours resulted in the precipitation of a black compound. The NO dissolved in the solution was driven off by nitrogen, then the precipitates were collected on a filter and washed with a small amount of water under a nitrogen stream. Three grams of a black, crystalline complex, I, were thus obtained.

Found: Co, 18.30; C, 29.91; H, 4.77; N, 21.69%. Calcd for $CoC_8H_{14}N_5O_5$: Co, 18.46; C, 30.10; H, 4.43; N, 21.95%. The same complex was obtained in a similar way in an acetone solution.

b) One gram of $Co(dmgH)_2$[3] was dissolved in 80 m*l* of methanol, and then NO was bubbled into the solution for about one hour with ice cooling, by which time the solution turned a brownish-black. After the remaining NO had been expelled with nitrogen, the solution was concentrated to 20 m*l* *in vacuo* at 50°C, thus leaving a crystalline precipitate of a brownish-black color. Yield: 0.5 g. The complex was proved to be identical with the complex I by a study of its IR spectral data.

Complex II: One gram of the complex I was quickly dissolved in 1 *l* of ether at room temperature, then the undissolved complex was filtered off. When the complex stood in air for a few minutes, yellowish-brown needles (complex II) were precipitated. Yield: 0.7 g.

Found: Co, 16.60; C, 27.08; H, 4.82; N, 19.51%. Calcd for $Co_2C_{16}H_{34}N_{10}O_{14}$: Co, 16.64; C, 27.12; H, 4.85; N, 19.78%. The complex II is soluble in methanol, tetrahydrofuran, and acetonitrile, but it is, unlike the complex I, sparingly soluble in benzene and insoluble in chloroform and ether.

The complex II was also obtained from a dichloromethane solution. One gram of the complex I was dissolved in 200 m*l* of dichloromethane, after which the solution was allowed to stand in air for about 24 hours (the solution had been concentrated to about 50 m*l*). Yellowish-brown needles, 0.7 g were thus separated. Elementary analysis and IR spectrum indicated the compound to be identical with the complex II obtained from ether solution.

Found: Co, 16.70; C, 27.22; H, 4.81; N, 19.84%. Calcd for $Co_2C_{16}H_{34}N_{10}O_{14}$: Co, 16.64: C, 27.12; H, 4.85; N, 19.78%.

Bis(dimethylglyoximato)nitroaquocobalt(III), $Co^{III}(dmgH)_2NO_2 \cdot OH_2$. One gram of the complex II was dissolved in a mixture of 150 m*l* of acetone and 10 m*l* of water. The solution was refluxed at 70—80°C for 10 hours, and then evaporated to 10 m*l* *in vacuo* to leave a brown precipitate (complex III). Yield: 0.8 g. This complex could be recrystallized from acetone.

Found: Co, 16.65; C, 27.34; H, 4.54; N, 20.00%. Calcd for $CoC_8H_{16}N_5O_7$: Co, 16.68; C, 27.20; H. 4.58; N, 19.83%. The complex III is soluble in methanol and acetonitrile, but insoluble in chloroform, ether, and benzene. The molecular weight, determined in an acetonitrile solution at 37°C by means of a Vapor Pressure Osmometer, was 341, corresponding to the value of 353 calculated on the basis of the above formula.

The complex III was also separated from an acetone solution of the complex II when it stood in air for two days.

The results of elementary analysis and the IR and UV spectral data agreed with those obtained for the same com-

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[1] For a comprehensive survey on transition metal nitrosyl complexes, see B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

[2] The following abbreviations are used in the present paper. dmgH: dimethylglyoximato monoanion, AE: bis(acetylacetone)-ethylenediiminato dianion, BE: bis(benzoylacetone)ethylenediiminato dianion, Salen: bis(salicylaldehyde)ethylenediiminato dianion, and dtc: *N,N*-dimethyldithiocarbamato monoanion.

[3] a) M. Tamaki, I. Masuda, and K. Shinra, This Bulletin, **42**, 2858 (1969). b) A. Earnshaw, P. C. Hewlett, and L. F. Larkwortly, *J. Chem. Soc.*, **1965**, 4718. c) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952); R. L. Carlin, F. Canziani, and W. K. Bratton, *J. Inorg. Nucl. Chem.*, **26**, 898 (1964).

[4] G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

pound prepared by Tschugaeff.[5)]

^{15}NO-, and ^{15}NO$_2$-Substituted Complexes. The (^{15}NO)-complex I was synthesized similarly by using ^{15}NO, generated from $K^{15}NO_3$ (97%).[6)] The (^{15}NO)(^{15}NO$_2$)-complex II and the (^{15}NO$_2$)-complex III were obtained from the (^{15}NO)-complex I. (^{15}NO)-complex I; Found: C, 29.01; H, 4.58; N, 21.92%. Calcd: C, 30.01; H, 4.42; N, 22.18%.

(^{15}NO)(^{15}NO$_2$)-complex II; Found: C, 26.84; H, 4.38; N, 19.02%. Calcd: C, 27.12; H, 4.85; N, 19.78%.

(^{15}NO$_2$)-complex III; Found: C, 27.33; H, 4.57; N, 19.91%. Calcd: C, 27.13; H, 4.56; N, 20.05%.

Measurements. The IR spectra were measured in Nujol or in hexachlorobutadiene, with 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 thermogravimetric analysis was carried out by using a Rigaku-denki thermobalance at a heating rate of 2°C/min under a nitrogen stream. The magnetic susceptibilities were measured at room temperature by the Gouy method. A nickel chloride solution was used as the calibrant. The electronic absorption spectra were obtained with a Hitachi EPS-3 spectrophotometer.

Results and Discussion

Complex I. The elementary analysis shows that the complex I has a composition corresponding to Co(dmgH)$_2$NO. The physical and chemical data, to be discussed below, agree with a structure where NO is bound axially to the central metal ion of the planar Co^{II}(dmgH)$_2$. As is seen in the IR spectrum in Fig. 1, Co(dmgH)$_2$NO shows an absorption band at 1641 cm^{-1} which can be assigned to the NO stretching frequency.[7)] The NO band observed in this region has been discussed as an indication of the neutral NO ligand in the complexes.[3a)] Upon replacing the NO ligand with ^{15}NO, this band shifts to 1615 cm^{-1} (Fig. 1 and Table 1). Besides the above band, the bands at 575 cm^{-1} and 540 cm^{-1} are also observed to shift slightly to lower wave numbers. The IR spectral feature of Co-(dmgH)$_2$NO in the 1600—700 cm^{-1} region resembles that of the planar, metal complexes including dimethylglyoximato, such as Ni^{II}(dmgH)$_2$,[8)] Cu^{II}(dmgH)$_2$,[9)] and [Co^{III}(dmgH)$_2$LL′](L,L′=Cl and/or NH$_3$).[9)]

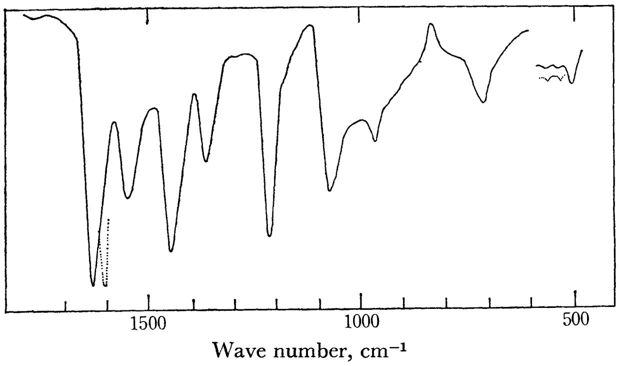

Fig. 1. IR spectra of Co^{II}(dmgH)$_2$NO (——) and Co (dmgH)$_2$-(^{15}NO) (······) in Nujol.

The electronic absorption spectrum of the complex measured in a chloroform solution is presented in Fig. 2. The spectrum shows an absorption band at 20×10^3 cm^{-1} with log ε ≒ 2.8. This band may be com-

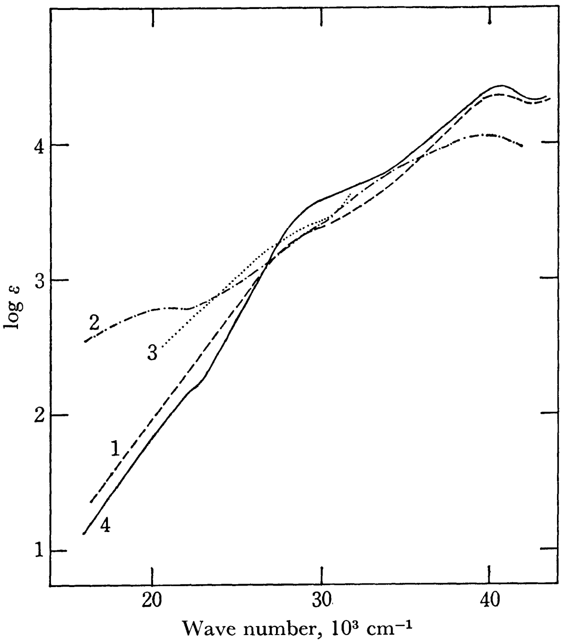

Fig. 2. Electronic spectra.
Co^{II}(dmgH)$_2$NO; curve 1 (- - -) in water, curve 2 (- · -) in CHCl$_3$, and curve 3 (······) in deaerated water. Co^{III}-(dmgH)$_2$NO$_2$·OH$_2$; curve 4 (——) in water.

Table 1. Characteristic frequencies in the IR spectra[a)] (cm^{-1})

	ν(NO)	ν_{as}(NO$_2$)	ν_s(NO$_2$)	δ(ONO)	ρ_w(NO$_2$)
Complex I:					
Co^{II}(dmgH)$_2$NO	1641				
Co^{II}(dmgH)$_2$(^{15}NO)	1615				
Complex II:					
[Co^{II}(dmgH)$_2$NO·OH$_2$][Co^{III}(dmgH)$_2$NO$_2$]·2H$_2$O	1628	1453	1322	820	618
[Co^{II}(dmgH)$_2$(^{15}NO)·OH$_2$][Co^{III}(dmgH)$_2$(^{15}NO$_2$)]·2H$_2$O	1600	1415	1301	812	603
Complex III:					
Co^{III}(dmgH)$_2$NO$_2$·OH$_2$		1453	1321	819	618
Co^{III}(dmgH)$_2$(^{15}NO$_2$)·OH$_2$		1416	1300	812	604

a) Obtained in Nujol and hexachlorobutadienes mulls at room temperature.

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8) R. Bling and D. Hadzi, *J. Chem. Soc.*, **1958**, 4536.

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parable to the band which has been taken as an indication of the square-pyramidal configuration of the complex, as in the cases of CoAE(NO),[3a] CoSalen(NO),[3a] or RCoSalen ($R=C_2H_5$ and C_6H_5),[10] though the assignment of these transitions has not yet been clarified. The diamagnetic property of the present complex is consistent with the above spectral data, both IR and electronic. Thus, this evidence has led us to propose a square-pyramidal configuration for the $Co(dmgH)_2NO$ complex.

As has been described in the Experimental part, $Co(dmgH)_2NO$ is easily converted into the complex III, which can be formulated as $Co(dmgH)_2NO_2 \cdot OH_2$. The molecular weight, 341, determined in acetonitrile, is consistent with this formula. The electronic spectra in an aqueous solution and the IR spectrum are identical with those of $Co^{III}(dmgH)_2NO_2 \cdot OH_2$,[11] which has been synthesized by Tschugaeff[5] in a different way. Four IR absorption bands, which are characteristic of the nitro group in the complexes,[12] $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, $\delta(ONO)$, and $\rho_w(NO_2)$ are assigned for the complex III at 1453, 1321, 819, and 618 cm^{-1} respectively (Fig. 3 and Table 1). The above assignments have been confirmed by the shifts of the bands to a lower frequency upon replacing the $^{15}NO_2$. It is worth noticing that the band for $\rho_w(NO_2)$ can clearly be assigned by ($^{15}NO_2$)-substitution indicating that the NO_2 group coordinates through nitrogen.[13]

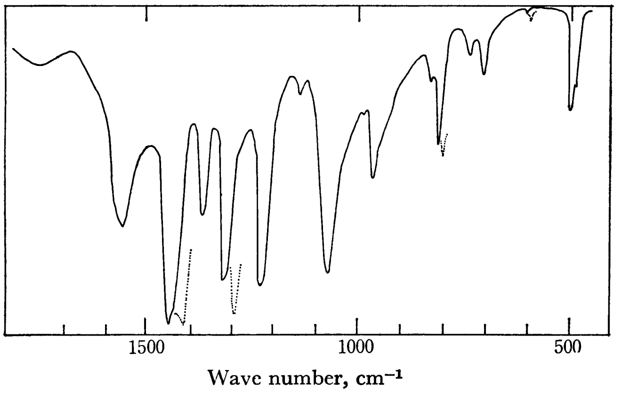


Fig. 3. IR spectra of $Co^{III}(dmgH)_2NO_2 \cdot OH_2$ (——) and $Co^{III}(dmgH)_2(^{15}NO_2) \cdot OH_2$ (······) in Nujol.

Conversion of NO into NO_2^-. It has been extensively studied how, in a series of six-coordinate Co(III) complexes including the NO_2 ligand, such as $[Co^{III}(NH_3)_5NO_2]Cl_2$, NO_2 exists as ONO^- in an alkaline solution and as NO_2^- in an acid solution.[14] This isomerization proceeds reversibly depending on the pH of the solution. As for the NO^+ ligand, it has been found, in the case of $[Fe^{II}(CN)_5NO]^{2+}$, that the NO^+ ligand is converted into ONO^- in an alkaline solution.[15,16] Recently, Godwin and Meyer reported the NO^+ ligand of $[Ru^{II}(bipy)_2(NO)X]^{2+}$ (X=Cl, Br) reacts with the hydroxide ion in an aqueous solution to form NO_2^-.[17] As far as the neutral NO ligand is concerned, no report has been presented dealing with the conversion of NO into ONO^- or NO_2^-, though many of the nitrosyl complexes have been synthesized where NO has been considered to be formally neutral.[3,18]

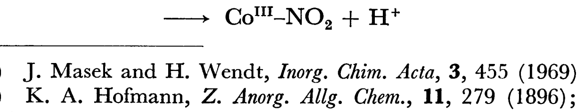
As has been described in the Experimental section, $Co^{II}(dmgH)_2NO$ (I) is very unstable in water and is rapidly oxidized to $Co^{III}(dmgH)_2NO_2 \cdot OH_2$(III). As may be seen in Fig. 2, the electronic spectrum of the complex I in an aqueous solution (curve 1) is quite different from that in chloroform (curve 2), but it is very close to the spectrum of the complex III in water (curve 4). These spectral data are thought to show that the conversion of the complex I into III takes place almost quantitatively. An oxygen-free, aqueous solution which was prepared by using a high vacuum line showed no absorption band at around 20×10^3 cm^{-1}. Upon exposing this solution to air, the solution came to show an absorption curve which is similar to the curve 1.

It may be said, from the above results, that, in an oxygen-free, aqueous solution, the complex I no longer preserves its penta-coordinate configuration and that both water and oxygen are consumed in the conversion reaction of the complex I to III.

TABLE 2. THE ν(NO) OF THE NITROSYL COMPLEXES (cm^{-1})

	a (in Nujol mull)	*b* (in CH_2Cl_2)	*b*–*a*
$Co(dmgH)_2NO$	1641	1705	64
$Co(dmgH)_2(^{15}NO)$	1615	1680	65
CoSalen(NO)	1624	1666	42
CoAE(NO)	1654	1650	−4
CoBE(NO)	1635	1653	18

An aqueous solution of the complex I shows acid: pH =4.35 for 2×10^{-3} M, implying that the conversion reaction includes the addition of the OH^- anion to the NO ligand, as in the case of the reaction of $[Fe^{II}(CN)_5NO]^{2+}$ forming $[Fe^{II}(CN)_5ONO]^{4+}$ in an alkaline solution.[15] As may be seen from Table 2, the NO stretching frequency of the complex I observed at 1641 cm^{-1} in Nujol shifts to 1705 cm^{-1} in CH_2Cl_2 solution; this shift is considerably larger than those observed for other nitrosyl complexes with similar structures. These data are considered to reflect a larger polarization, as $(Co^{II})^{\delta-}$—$(N{=}O)^{\delta+}$ in the present complex, which may facilitate the OH^- addition, as is shown in Scheme (I).



$$(Co^{II})^{\delta-}\text{-}(NO)^{\delta+} + OH^- \longrightarrow \left[Co^{II}\text{-}N\begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix} \right]^- \longrightarrow Co^{III}\text{-}NO_2 + H^+ \qquad (I)$$

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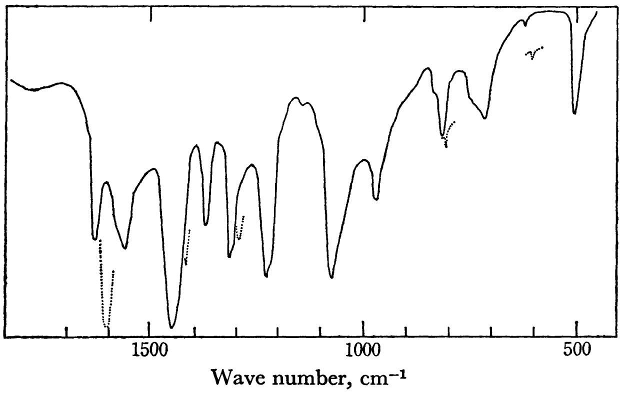

Fig. 4. IR spectra of $[Co^{II}(dmgH)_2NO \cdot OH_2]$ $[Co^{III}(dmgH)_2NO_2] \cdot 2H_2O$ (——) and $[Co^{II}(dmgH)_2(^{15}NO) \cdot OH_2][Co^{III}(dmgH)_2(^{15}NO_2)] \cdot 2H_2O$ (······) in Nujol.

Complex II. This compound was separated as a crystalline precipitate during the conversion of the complex I into the complex III in an ether solution. The complex II is diamagnetic, and the results of elementary analysis are in fair agreement with the $Co_2(dmgH)_4NO \cdot NO_2 \cdot 3H_2O$ composition. In the thermogravimetric analysis curve for the complex II, the weight loss of about 8.5% observed between 145—165°C is thought to correspond to the loss of three water molecules in the complex. Unlike the complex I, the complex II is insoluble in chloroform and ether. The complex exhibits the characteristic bands for both NO_2 and NO, as may be seen in Fig. 4 and Table 1. Each of the four bands for NO_2 is observed at almost the same frequency as for the complex III; the NO band is found to be slightly shifted to a lower frequency than in the complex I. These facts can hardly be understood without proposing that both the NO_2 and NO groups are involved in the complex. Thus, the structure of the complex II seems to include either a Co—Co bond or an NO bridge. The possible formation of a Co—Co bond by the interaction between Co(II) complexes with a low-spin d^7 configuration has been reported for $[Co^{II}(dmgH)_2B]_2$ where B is pyridine, aquo or triphenylphosphine.[4, 19] However, in the case of a diamagnetic complex such as $Co(dmgH)_2NO$, it is difficult to expect a similar Co—Co bond. With respect to the complexes with bridging NO, it has been reported that the NO band is observed at about 1500 cm^{-1} for $(C_5H_5)_3Mn(NO)_3$ and $[C_5H_5Cr(NO)_2]_2$.[20] The fact that the present complex shows the NO band at 1628 cm^{-1}, only slightly shifted to a lower frequency than that (1641 cm^{-1}) of the complex I, does not indicate clearly the existence of a bridging NO group. A very weak interaction through the NO group may be supposed to take place in the complex II.

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