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# Chelating Nitrite Groups in Some Cobalt(II) Complexes[1]

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Complexes of the type $CoL_2(NO_2)_2$, where L represents a substituted pyridine N-oxide or a substituted quinoline N-oxide, were prepared and studied. Infrared and electronic spectra have shown that the complexes are six-coordinate with chelating nitrite groups. Steric effects as well as basic strength of the ligands appear to be factors which lead to chelation of the nitrite groups.

## Introduction

As a bidentate ligand, the nitrite group is capable of bonding to metal ions in two distinct ways: by forming bridges between two metal ions through the nitrogen and one oxygen atom, or by chelating through the two oxygen atoms to one metal ion. Only a few complexes of palladium(II) and cobalt(III) with $NO_2$ bridges have been characterized.[2] The first example of a chelating $NO_2$ group was recently discovered by Goodgame[3] in some cobalt(II) and nickel(II) nitrite complexes. The presence of chelating nitrite groups in the nickel complexes was explained as due to the tendency of nickel(II) to attain a coordination number of six with more favorable bond energy resulting from the four Ni–O bonds than from two Ni–$NO_2$ bonds. No explanation was given as to why the nitrite group would chelate with Co(II). Since this was the first reported work, it was of importance to prepare additional Co(II) complexes in order to determine factors which would influence the formation of chelating $NO_2$ groups. In the present work cobalt(II) nitrite complexes with dimethylpyridine N-oxides or lutidine N-oxides (LNO), trimethylpyridine N-oxide or collidine N-oxide (CNO), 2- and 4-methylquinoline N-oxides (2- and 4-MeQNO) were studied.

## Experimental Section

**Materials.**—2-Methylpyridine N-oxide and 2,6-lutidine N-oxide were available commercially from Aldrich Chemical Co. The other amine N-oxides were prepared from the corresponding amines by oxidation with hydrogen peroxide and acetic acid using the method of Ochiai.[4]

**Preparation of $CoL_2Cl_2$ (L = Amine N-Oxide).**—The cobalt(II) chloride complexes were prepared by methods described in the literature.[5]

**Preparation of $CoL_2(NO_2)_2$.**—The cobalt(II) nitrite complexes were obtained by treating the solution of $CoL_2Cl_2$ in dry acetone with twofold excess of very finely powdered silver nitrite.[3] The blue solution of the cobalt(II) chloride complexes turned mauve after a few minutes of vigorous shaking. The solutions were filtered and then evaporated under vacuum until mauve crystals formed.

**Co(2,4-LNO)$_2$(NO$_2$)$_2$** gave a mauve oil after evaporation of the acetone and was triturated several times with ether until crystals formed. The mauve crystals were contaminated with brown residue. The crude product was redissolved in the minimum amount of acetone and treated with a few drops of ether. When brown solid settled, the supernatant mauve solution was concentrated and the crystals formed upon addition of ether. The compound was filtered and dried under vacuum. *Anal.* Calcd for $C_{14}H_{18}N_4CoO_6$: C, 42.32; H, 4.56; N, 14.10. Found: C, 42.20; H, 4.84; N, 13.45.

**Co(2,4,6-CNO)$_2$(NO$_2$)$_2$.**—A light mauve compound was obtained from the concentrated acetone solution. *Anal.* Calcd for $C_{16}H_{22}N_4CoO_6$: C, 45.18; H, 5.21; N, 13.17. Found: C, 44.04; H, 5.42; N, 12.95.

**Co(2,6-LNO)$_2$(NO$_2$)$_2$.**—Mauve crystals were obtained upon concentration of the acetone solution. *Anal.* Calcd for $C_{14}H_{18}N_4CoO_6$: C, 42.32; H, 4.56; N, 14.10. Found: C, 42.55; H, 4.92; N, 14.05.

**Co(4-MeQNO)$_2$(NO$_2$)$_2$.**—Dark mauve crystals were formed upon concentration of the acetone solution. *Anal.* Calcd for $C_{20}H_{18}N_4CoO_6$: C, 51.18; H, 3.86; N, 11.94. Found: C, 50.82; H, 3.94; N, 11.22.

**Co(2-MeQNO)$_2$(NO$_2$)$_2$.**—Dark mauve crystals were obtained from the acetone solution. *Anal.* Calcd for $C_{20}H_{18}N_4CoO_6$: C, 51.18; H, 3.86; N, 11.94. Found: C, 50.63; H, 3.92; N, 11.40.

The 2-methylpyridine N-oxide, 3,5-lutidine N-oxide, and quinoline N-oxide gave unstable cobalt(II) nitrite complexes. The mauve solutions turned brown upon concentration by solvent evaporation.

**Physical Measurements.**—The infrared spectra were obtained on a Beckman IR-4 spectrophotometer equipped with sodium chloride optics. An expanded scale (0.1 $\mu$/in.) was used to determine more precisely the position of the bands. Calibration was made using a polystyrene film.

The electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. The Nujol mull spectra were obtained using the technique developed by Lee, Griswold, and Kleinberg.[6]

The magnetic susceptibilities were determined by the Faraday method. Mercury(II) tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard.

**Chemical Analyses.**—C, H, and N analyses were performed by Alfred Bernhardt, Mikroanalytischen Laboratory, Mülheim (Ruhr), Germany.

## Results and Discussion

The well-known tetrahedral cobalt(II) complexes are usually blue,[7-10] in contrast with the octahedral complexes which are generally pink or violet.[11-14]

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Cobalt(II) chloride complexes with 2,6- and 3,5-lutidine N-oxides and the quinoline N-oxides were blue. The electronic spectra of these complexes are similar to those reported for Co(2,4-LNO)$_2$Cl$_2$ and Co(2,4,6-CNO)$_2$Cl$_2$ which were shown to be tetrahedral in the solid state.[5] As a result it is concluded that the chloride complexes with the amine N-oxides are tetrahedral. The cobalt(II) nitrite complexes are mauve in color which suggests that they are octahedral.

Magnetic moment measurements have been used as criteria for the stereochemistry of cobalt(II) complexes. The data for the cobalt(II) nitrite compounds are given in Table I. The values agree closely with those reported for Co[(CH$_3$)$_3$PO]$_2$(NO$_3$)$_2$, Co[(C$_6$H$_5$)$_3$PO]$_2$(NO$_3$)$_2$, and Co[(C$_6$H$_5$)$_3$AsO]$_2$(NO$_3$)$_2$.[15] In these complexes Co(II) is six-coordinate with chelating nitrate groups. An X-ray study of dinitratobis(trimethylphosphine oxide)cobalt(II) showed that the cobalt is surrounded by an irregular arrangement of six oxygen atoms.[16]

TABLE I

MAGNETIC DATA OF THE COBALT(II) NITRITE COMPLEXES

| Compound | Magnetic Susceptibilities at 298°K | | |
|---|---|---|---|
| | $10^6\chi_m$ | $10^6\chi_m^{cor}$ | $\mu_{eff}$, BM |
| Co(2,4-LNO)$_2$(NO$_2$)$_2$ | 8786 | 8989 | 4.63 |
| Co(2,6-LNO)$_2$(NO$_2$)$_2$ | 8940 | 9143 | 4.67 |
| Co(2,4,6-CNO)$_2$(NO$_2$)$_2$ | 7760 | 7986 | 4.36 |
| Co(2-MeQNO)$_2$(NO$_2$)$_2$ | 8324 | 8563 | 4.52 |
| Co(4-MeQNO)$_2$(NO$_2$)$_2$ | 8708 | 8947 | 4.62 |

**Infrared Spectra.**—The nitrite ion has three fundamental vibrational modes which are infrared active. These belong to the asymmetric stretching $\nu_{as}$, the symmetric stretching $\nu_s$, and the bending mode $\nu_b$. The number of infrared-active modes does not change upon coordination but they are shifted as compared to the free ion frequencies. The shifts of $\nu_{as}$(NO$_2$) and $\nu_s$(NO$_2$) are of interest in the determination of the mode of bonding of the nitrite group.

Bands assigned to the NO$_2$ groups in the cobalt complexes are listed in Table II. These bands were easily identified by comparing the spectra of the cobalt nitrite complexes with their analogous cobalt chloride compounds. As shown in the table, both $\nu_{as}$(NO$_2$) and $\nu_s$(NO$_2$) are shifted to lower frequencies than in the free nitrite ion. In complexes with NO$_2$ bridges,[2] $\nu_{as}$(NO$_2$) is raised to higher values, whereas $\nu_s$(NO$_2$) is lowered. Therefore it is suggested that the nitrite groups in the cobalt complexes are chelating with both oxygen atoms coordinating to the metal ion. Such chelation reduces the bond order of the two N–O bonds and hence both $\nu_{as}$(NO$_2$) and $\nu_s$(NO$_2$) appear at lower frequencies.[3] This is contrasted to nitro complexes where both $\nu_{as}$(NO$_2$) and $\nu_s$(NO$_2$) are shifted to higher frequencies as compared to the free nitrite ion.[2,17–19] The frequencies for the chelating NO$_2^-$ ion are different than for the nitrito complexes as the asymmetric stretching vibration lies at higher and the symmetric stretching frequencies at lower values than the free-ion frequencies.[17,20,21]

TABLE II

NO$_2^-$ FREQUENCIES (CM$^{-1}$) OF CoL$_2$(NO$_2$)$_2$

| Compound[a] | $\nu_{as}$ | $\nu_s$ | $\nu_b$ |
|---|---|---|---|
| NaNO$_2$[b,c] | 1328 ± 2 m | 1261 ± 3 vs | 828 ms |
| Co(2,4-LNO)$_2$(NO$_2$)$_2$ | 1292 ms | 1201[d] | 859 ms |
| Co(2,6-LNO)$_2$(NO$_2$)$_2$ | 1278 ms | 1207 vs | 859 ms |
| Co(2,4,6-CNO)$_2$(NO$_2$)$_2$ | 1292 ms | 1219 vs | 858 ms |
| Co(2-MeQNO)$_2$(NO$_2$)$_2$ | 1317 ms | 1202 vs | 830 m |
| Co(4-MeQNO)$_2$(NO$_2$)$_2$ | 1281 sh | 1214 vs | 856 m |

[a] As Nujol and hexachlorobutadiene mulls. [b] See ref 2. [c] R. E. Weston and T. F. Brodasky, *J. Chem. Phys.*, **24,** 683 (1957). [d] Band not assigned with certainty due to strong absorption of the N-oxide of the ligand in this region.

TABLE III

ABSORPTION MAXIMA IN THE VISIBLE AND NEAR-INFRARED REGION

| Compound | State | Abs maxima, m$\mu$ ($\epsilon_{molar}$ for soln) |
|---|---|---|
| Co(2,4-LNO)$_2$(NO$_2$)$_2$ | Mull | 525, 700 w, 1130 br |
| | Acetone | 540 (131), 710 (18.5), 1130 br (23.5) |
| Co(2,6-LNO)$_2$(NO$_2$)$_2$ | Mull | 520, ~710 sh, 1140 br |
| | Acetone | 535 (96), 710 (12), 1140 br (17) |
| Co(2,6-LNO)$_2$(NO$_3$)$_2$[22] | Solid in LiF | 525, 710 br, 1100 |
| Co(2,4,6-CNO)$_2$(NO$_2$)$_2$ | Mull | 535, ~700 w, 1130 br |
| | Acetone | 535 (126), 710 (21.5), 1130 br (28) |
| Co(2,4,6-CNO)$_2$(NO$_3$)$_2$[22] | Solid in LiF | 520, 710, 1100 br |
| Co(2-MeQNO)$_2$(NO$_2$)$_2$ | Mull | 462, 486, 522, 100, 1150 |
| | Acetone | ~460 sh, 486 (115), 520 (110), 700 (12), 1160 (12) |
| Co(4-MeQNO)$_2$(NO$_2$)$_2$ | Mull | 466, 500, 530, 700, 1170 |
| | Acetone | ~460 sh, 502 (170), 530 sh, ~700 sh, 1150 (16) |

**Electronic Spectra.**—Both the mull and the solution spectra of the cobalt(II) nitrite complexes were obtained. The band maxima are listed in Table III and the solution spectra of Co(2,6-LNO)$_2$(NO$_2$)$_2$, Co(2-MeQNO)$_2$(NO$_2$)$_2$, and Co(4-MeQNO)$_2$(NO$_2$)$_2$ are shown in Figure 1. The electronic spectra of Co(2,6-LNO)$_2$(NO$_2$)$_2$ and Co(2,4,6-CNO)$_2$(NO$_2$)$_2$ are very similar to those of the analogous cobalt nitrate complexes which were shown to be six-coordinate complexes with bidentate nitrate groups.[22] The mull spectra are very similar to the solution spectra thus indicating that the complexes are fairly stable in acetone as a solvent. The absorption maxima differ both in position and intensity from those of tetrahedral cobaltous complex ion.[7,10] The band intensities, however, are appreciably greater than those of typical octahedral complexes.[23] Similar

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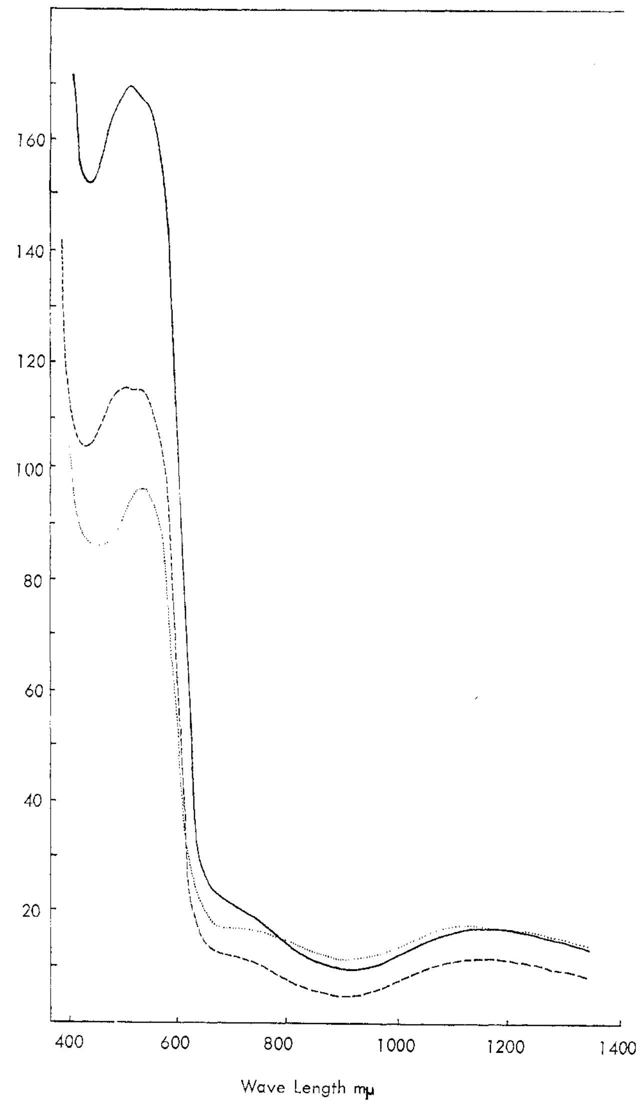

Figure 1.—Solution spectra of $Co(4\text{-}MeQNO)_2(NO_2)_2$ (———), $Co(2\text{-}MeQNO)_2(NO_2)_2$ (– – – –), and $Co(2,6\text{-}LNO)_2(NO_2)_2$ (· · · ·) in acetone.

intensities were found in six-coordinate cobalt(II) nitrate complexes studied by Cotton and co-workers.[15]

In the complex $Co[(CH_3)_3PO]_2(NO_3)_2$, the bidentate nitrate ligand has a bond angle (O–Co–O) of 57.2° with cobalt.[16] Similarly a small bond angle between the cobalt and the two oxygens of the nitrite chelate would be expected. Such arrangement of the six-coordinated oxygens about cobalt would lead to considerable distortion. This structure could approach a distorted tetrahedral array.[15] On this basis, the low magnetic moments and high absorption band intensities of the cobalt nitrite complexes can be explained. An examination of these data suggests two factors which influence the chelating structure of the nitrite group. These two factors are the size of the amine N-oxides and their coordinating ability. The complexes with chelating nitrito or nitrato groups were formed with bulky ligands, such as $(C_6H_5)_3PO$, $(CH_3)_3PO$, $(C_6H_5)_3AsO$,[3,15] and the ligands used in this study. The basicity of the ligand is a very important factor. The 3,5-lutidine N-oxide and the quinoline N-oxide which form tetrahedral cobalt chloride complexes in the solid state gave very labile nitrite complexes. The mauve solutions turned brown upon concentration by solvent evaporation, probably owing to solvolysis. The 3,5-lutidine N-oxide is less basic than the 2,4- and 2,6-lutidine N-oxides.[24] The insertion of a methyl group in the 2 or 4 position of quinoline N-oxide increases its basic strength[25] and helps to yield stable nitrite complexes.

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