# Five-coordinate Bis(8-aminoquinoline) Nitrosylcobalt Complexes

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$[Co(C_9H_8N_2)_2NO]X_2 \cdot nH_2O$ ($C_9H_8N_2$=8-aminoquinoline; X=Cl, Br, I, $NO_3$, $ClO_4$, and $SO_4/2$; $n$=0, 1, 1.5, and 2) was isolated by the reaction of nitrogen oxide with a mixture of the corresponding cobalt(II) salt and 8-aminoquinoline in methanol. The IR, UV, and molar conductivity measurements suggest that the geometry of the cation is a tetragonal pyramid with an apical $NO^-$.

Nast *et al.* reported that paramagnetic deep blue compounds formulated as $[Co(C_9H_8N_2)_2NO]X_2$ ($C_9H_8N_2$=8-aminoquinoline; X=Cl and $NO_3$) had been isolated by the reaction of nitrogen oxide with $CoX_2(C_9H_8N_2)_2$ in methanol, and that the geometry of the complex cation was a tetragonal pyramid with an apical $NO^-$, its N–O stretching vibration being assigned to a *ca.* 1170 $cm^{-1}$ band.[1] Subsequently, it was established that N–O stretching vibrations for nitrosylcobalt complexes with this geometry can be observed in the region 1620—1710 $cm^{-1}$ and most of the compounds are diamagnetic.[2,3] N–O stretching vibrations for compounds bridged by a NO group and those for compounds containing an anion of dimer of nitrosyl group such as a hyponitrite ion were observed in the region 1300—1550 and 920—1270 $cm^{-1}$, respectively.[4,5]

The authors reinvestigated the reaction of nitrogen oxide with $CoX_2(C_9H_8N_2)_2$ to make clear the detals. In this paper, they report the syntheses and characterization of some new five-coordinate mononitrosyl complexes which are different from the compounds isolated by Nast *et al.*[1]

## Experimental

*Preparations.* The compounds were prepared by the use of a Schlenk apparatus under nitrogen atmosphere. Four mmol of 8-aminoquinoline was added to *ca.* 50 $cm^3$ of deoxygenated methanol solution containing 2 mmol of cobalt(II) salt to give a deep orange solution. Nitrogen oxide (of purity more than 99.0%) purchased from Seitetsu Kagaku Co., Ltd., after being further purified by passing it through a trap at −80 °C, was then passed into this solution at room temperature causing the solution to darken gradually with the formation of a precipitate. This precipitation was not reported by Nast *et al.*[1] After the nitrogen oxide had been replaced with nitrogen, the precipitate was collected by filtration, washed with methanol and diethyl ether, successively in air, and dried over anhydrous calcium chloride under vacuum. Yield, 500—700 mg. The elementary analyses are given in Table 1. The filtrate was wine red. The same compounds could also be prepared by the reaction of $CoX_2(C_9H_8N_2)_2$ with the nitrogen oxide in methanol, but could not be prepared by exposure of $CoX_2(C_9H_8N_2)_2$ in the solid state to the nitrogen oxide under *ca.* 1 atmosphere at room temperature. The $^{15}NO$($^{15}N$ atom%=95.5) analogues were prepared in a vacuum system on a scale half of the ordinary one by the use of *ca.* 3 mmol of $^{15}NO$ derived from $K^{15}NO_3$.

The wine red filtrate was dropped into a large volume of petroleum ether or diethyl ether (*ca.* 500 $cm^3$), while being stirred, to give the paramagnetic deep blue precipitate reported by Nast *et al.*[1]

$[CoNO(diars)_2](ClO_4)_2$ (diars=1,2-bis(dimethylarsino)benzene), $[CoINO(diars)_2]ClO_4$, and their $^{15}NO$-substituted compounds were synthesized by the use of a vacuum system in accordance with Ref. 6.

*Measurements.* The magnetic susceptibility was measured by the Gouy method. The IR spectra were measured as Nujol and hexachlorobutadiene mulls in the region 200—4000 $cm^{-1}$ on JASCO 402G and JASCO IR-F spectrometers. The wave numbers of the observed bands were calibrated with polystyrene film and water vapor. The UV spectra in *N,N*-dimethylformamide were measured with a Hitachi 124 spectrometer and the diffuse reflection spectra with a Hitachi EPS-3T spectrometer. The molar conductivities in *N,N*-dimethylformamide were measured in the range $(2.5—10)\times10^{-3}$ M at 25 °C (±0.1 °C) with a universal bridge (Model 4225A of Yokogawa-Hewlett-Packard Ltd.). The *N,N*-dimethylformamide was purified by the standard method, its electrolytic conductivity being $(1.1—2.3)\times10^{-5}$ S $m^{-1}$.

## Results and Discussion

*Properties of the Compounds.* All the compounds obtained were stable in air, and were soluble in water, methanol, and ethanol to give wine red solutions from which the deep blue compounds reported by Nast *et al.*

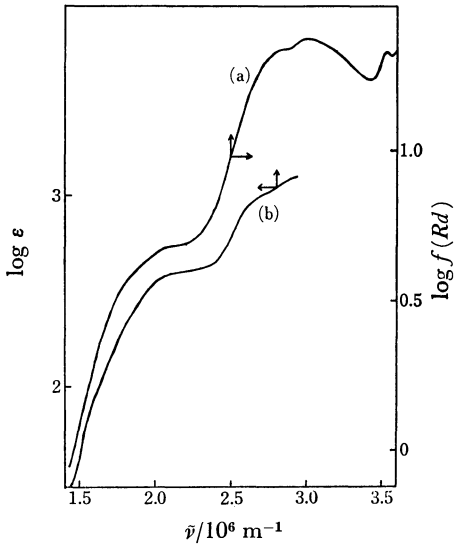


Fig. 1. UV spectra of $[Co(C_9H_8N_2)_2NO](NO_3)_2$; a: in *N,N*-dimethylformamide($1.266\times10^{-4}$ M), b: in the solid state.

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Table 1. Elementary analyses of the compounds

| Compound | | Co | C | H | N | Halogen | $H_2O$ | S/% |
|---|---|---|---|---|---|---|---|---|
| $[Co(C_9H_8N_2)_2NO]Cl_2\cdot 2H_2O$ (khaki) | Calcd | 12.17 | 44.65 | 4.16 | 14.46 | 14.65 | | |
| | Found | 12.2 | 47.29 | 4.23 | 14.43 | 14.49 | | |
| $[Co(C_9H_8N_2)_2NO]Br_2\cdot 2H_2O$ (brown) | Calcd | 10.28 | 37.72 | 3.52 | 12.23 | 27.88 | | |
| | Found | 10.5 | 40.18 | 3.60 | 12.05 | 27.65 | | |
| $[Co(C_9H_8N_2)_2NO]I_2\cdot H_2O$ (chocolate) | Calcd | 9.08 | 33.31 | 2.79 | 10.78 | 39.10 | 2.78 | |
| | Found | 9.06 | 33.28 | 2.76 | 10.39 | 38.35 | 3.08 | |
| $[Co(C_9H_8N_2)_2NO](ClO_4)_2$ (russet) | Calcd | 10.23 | 37.52 | 2.80 | 12.15 | 12.31 | | |
| | Found | 10.4 | 37.48 | 2.81 | 12.27 | 12.28 | | |
| $[Co(C_9H_8N_2)_2NO](NO_3)_2$ (dark brown) | Calcd | 11.75 | 43.13 | 3.22 | 19.56 | | | |
| | Found | 11.9 | 43.41 | 3.32 | 19.22 | | | |
| $[Co(C_9H_8N_2)_2NO]SO_4\cdot 1.5H_2O$ (khaki) | Calcd | 11.78 | 43.21 | 3.83 | 14.00 | | 5.40 | 6.41 |
| | Found | 11.8 | 42.77 | 3.71 | 13.93 | | 5.34 | 6.17 |
| $[Co(C_9H_8N_2)_2NO]SO_4\cdot H_2O$[a] (khaki) | Calcd | 11.99 | 44.00 | 3.69 | 14.25 | | 3.67 | 6.52 |
| | Found | 12.0 | 43.11 | 3.58 | 14.03 | | 3.64 | 6.12 |

a) This compound could be obtained from $[Co(C_9H_8N_2)_2NO]SO_4\cdot 1.5H_2O$ by drying it over $P_4O_{10}$ in vacuum.

Table 2. IR data and molar conductivities of the compounds

| Compound | $\nu$NO / $cm^{-1}$ | $\delta$CoNO / $cm^{-1}$ | $\nu$CoN / $cm^{-1}$ | $\Lambda$[a] / $10^{-4}$ S $m^2$ $mol^{-1}$ | Slope[b] | Electrolyte type |
|---|---|---|---|---|---|---|
| $[CoCl(en)_2NO]ClO_4$ | | | | 153 | 560 | 1:1 |
| $[Ru(phen)_3]I_2\cdot H_2O$ | | | | 244 | 1200 | 2:1 |
| $[Co(phen)_3]Br_3$ | | | | 356 | 3120 | 3:1 |
| $[Co(C_9H_8N_2)_2NO[Cl_2\cdot 2H_2O$ | 1651 vs (26)[c] | 520 w(8) | 308 sh? | e) | | |
| $[Co(C_9H_8N_2)_2NO]Br_2\cdot 2H_2O$ | 1662 vs (28) | 520 w(8) | 305 w(4) | 171 | 1180 | 2:1 |
| $[Co(C_9H_8N_2)_2NO]I_2\cdot H_2O$ | 1670 vs | 517 sh? | d) | 230 | 950 | 2:1 |
| $[Co(C_9H_8N_2)_2NO](ClO_4)_2$ | 1715 vs (29) | 501 w(4)? | d) | 275 | 1230 | 2:1 |
| $[Co(C_9H_8N_2)_2NO](NO_3)_2$ | 1683 vs (29) | 520 w(6) | d) | 253 | 1470 | 2:1 |
| $[Co(C_9H_8N_2)_2NO]SO_4\cdot 1.5H_2O$ | 1635 vs, br | d) | d) | e) | | |
| $[Co(C_9H_8N_2)_2NO]SO_4\cdot H_2O$ | 1632 vs, br | d) | d) | e) | | |

a) Molar conductivities at $2.5\times 10^{-3}$ M. b) $(\Lambda_0-\Lambda)/\sqrt{C}$ where $\Lambda_0$ is molar conductivity at infinite dilution, $\Lambda$ being that at $C$ mol/$dm^3$. c) The value in parentheses indicates observed $^{15}N$-isotopic shift. d) Not observed. e) Unstable in *N,N*-dimethylformamide. $\nu$NO, N–O stretching vibration. $\delta$CoNO, Co–N–O bending vibration. $\nu$CoN, Co–N stretching vibration. vs, very strong; w, weak; sh, shoulder; br, broad.

precipitate by addition of petroleum ether or diethyl ether. UV spectra of the wine red solutions were consistent with those of the deep blue compounds. All of the compounds except the chloride and sulfate were stable in *N,N*-dimethylformamide for a few hours. Although they could not be purified by recrystallization from *N,N*-dimethylformamide, they gave excellent results for the elementary analyses.

Magnetic susceptibilities, $\chi_g$, for the chloride, bromide, iodide, perchlorate, and nitrate are $-0.38$, $+1.33$, $-0.06$, $+0.01$, and $-0.14\times 10^{-6}$ $cm^3$ $g^{-1}$, respectively. Thus, all the compounds are essentially diamagnetic. The slight paramagnetism is probably due to contamination by a small amount of the deep blue compound ($\mu_B=3.45$ and 2.95 B. M. for the chloride and nitrate, respectively) reported by Nast *et al.* considering the synthetic conditions.

*UV Spectra and Molar Conductivities.* The spectral figures in *N,N*-dimethylformamide are similar to those of the diffuse reflection as shown in Fig. 1. Hence, the structures of the cation in the solid state of the bromide, iodide, perchlorate, and nitrate may be the same as those in *N,N*-dimethylformamide. The UV spectra in *N,N*-dimethylformamide show a peak or shoulder at $(1.9—2.1)\times 10^6$ $m^{-1}$ with log $\varepsilon=2.7—2.8$, which is a characteristic band of a tetragonal pyramid-type nitrosyl complex with an apical $NO^-$ group.[2]

The measurement of the molar conductivity was carried out within *ca.* one hour after the compounds had been dissolved. The molar conductivities were compared with those of 3:1-, 2:1-, and 1:1-type electrolytes by the method of Feltham and Hayter.[7] The results in Table 2 show that the compounds are 2:1-type electrolytes.

*IR Spectra.* The wave numbers and their assignments due to the CoNO group are summarized in Table 2.

No isotopic shift upon $^{15}NO$-substitution was observed in the bands at *ca.* 1100 $cm^{-1}$, while the bands at 1630—1720 $cm^{-1}$ shifted downwards by 26—29 $cm^{-1}$. Hence, the latter can be assigned to the N–O stretching vibrations.

The isotopic shift in the region 200—700 $cm^{-1}$ was carefully measured because a number of bands due to 8-aminoquinoline disturbed the assignments of skeletal vibrations due to the CoNO group. The 500—520 $cm^{-1}$ bands showed the isotopic shift, its value being 4—8 $cm^{-1}$. The 305 $cm^{-1}$ band for the bromide shifted to 301 $cm^{-1}$; however, no band in the region of 300 $cm^{-1}$ was observed for the other compounds. This can be

explained from the fact that a very strong band at 290—300 $cm^{-1}$ due to the coordinated 8-aminoquinolines overlapped the bands due to the CoNO group.

For nitrosylcobalt complexes, the N–O stretching vibration of the $NO^-$ complex is observed in the region 1570—1710 $cm^{-1}$, while that of the $NO^+$ complex such as $[CoNO(diars)_2](ClO_4)_2$ at 1846 $cm^{-1}$.[2,3,6,8] The $^{15}N$-isotopic shift of the N–O stretching vibration for $[CoNO(diars)_2](ClO_4)_2$ was 36 $cm^{-1}$, this value being quite similar to the isotopic shift, 35 $cm^{-1}$, calculated by a linear Co–N–O arrangement. On the other hand, the isotopic shift of the N–O stretching vibrations for the $NO^-$ complexes such as $[Co(NH_3)_5NO]Cl_2$ ($\nu$NO, 1614 $cm^{-1}$), $[Co(OClO_3)(en)_2NO]ClO_4$ ($\nu$NO, 1661 $cm^{-1}$), $Co\{S_2CN(CH_3)_2\}_2NO$ ($\nu$NO, 1624 $cm^{-1}$), and $[CoINO(diars)_2]ClO_4$ ($\nu$NO, 1575 $cm^{-1}$) was in the range 25—29 $cm^{-1}$.[9] Thus, the value of the $^{15}N$-isotopic shift for the N–O stretching vibration is sensitive to the metal–N–O bond angle.

Skeletal vibrations of the metal–N–O group are observed in the wide region 280—600 $cm^{-1}$, which have been established from the $^{15}NO$-substitution.[9] For $NO^+$ complexes, the skeletal vibrations are observed in the limited region *ca.* 450—650 $cm^{-1}$. For example, those for $[CoNO(diars)_2](ClO_4)_2$ in the present work were observed at 477 and 501 $cm^{-1}$, the $^{15}N$-isotopic shifts being 10 and 11 $cm^{-1}$, respectively. For $NO^-$ complexes, the metal–N stretching and the metal–N–O bending vibrations are observed in the regions, 280—340 and 500—620 $cm^{-1}$, respectively, and the $^{15}N$-isotopic shift for the former vibration is generally smaller than that for the latter one. Thus, the 500—520 $cm^{-1}$ bands for the present compounds can be assigned to the Co–N–O bending and the *ca.* 300 $cm^{-1}$ bands to the Co–N stretching vibrations. Similar vibrational frequencies are also observed in a strongly bent nitrosyl, XNO (X= F, Cl, and Br); the X–N–O bending vibrations appear in the region 550—780 $cm^{-1}$, the X–N stretching vibrations in the region 270—520 $cm^{-1}$. The $^{15}N$-isotopic shift of the X–N–O bending vibration is 14—18 $cm^{-1}$, that of the X–N stretching one being 2.2—2.5 $cm^{-1}$.[10]

The position of the N–O stretching vibration, its $^{15}N$-isotopic shift, and the far IR measurement suggest that the present compounds are formulated as $NO^-$ complex.

IR bands due to the stretching vibration of Co–X (X=Cl, Br, and I) are usually observed in the region 170—350 $cm^{-1}$, and the bands due to the Co–O stretching vibration resulted from coordination of perchlorate, nitrate, and sulfate ions to the cobalt atom in the region 200—350 $cm^{-1}$.[11,12] Spectral figures in the region 200—350 $cm^{-1}$ for the compounds were very similar to each other. This finding supports the contention that the anions are not in the coordination sphere, which is also suggested from the molar conductivity measurements.

It is well known that geometry of five-coordinate mononitrosyl complexes with a CoNO group, the formal oxidation state of which is II, is divided into two forms: a tetragonal pyramid with an apical $NO^-$ and a trigonal bipyramid with an equatorial $NO^+$.[3] From the experimental results, the geometry of the cation of the present compounds is considered to be a tetragonal pyramid with an apical $NO^-$.

The compounds reported in this paper may be a precursor of the deep blue compounds isolated by Nast *et al.*[1] considering the synthetic conditions and the properties of the compounds.

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