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## Ligand Effects on the Bonding Mode of the Cyanate Ion in Complexes of Copper(II) and Nickel(II) <sup>1</sup>

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The results of an investigation of the bonding mode of the cyanate ion in complexes of copper(II) and nickel(II) containing 4-substituted pyridine derivatives and various other aromatic  $\pi$ -acceptor amines indicate that the bonding mode of the cyanate is rather insensitive to the electronic environment in these complexes and continues to bond through the nitrogen atom. Infrared and VIS-UV spectral data indicate that the  $[\text{CuL}_2(\text{NCO})_2]$  complexes generally involve square planar geometry with trans monodentate ligands (cis, of course, with bidentate ligands) and the  $[\text{NiL}_4(\text{NCO})_2]$  complexes are trans octahedral (except for cis- $[\text{Ni}(1,10\text{-phenanthroline})_2(\text{NCO})_2]$ ). Significant exceptions to these generalizations include  $[\text{Cu}(4\text{-pyridinealdoxime})_2(\text{NCO})_2]$ , which is believed to exhibit octahedral geometry due to bridging aldoxime groups;  $[\text{Cu}(\text{quinoline})_2(\text{NCO})_2]$  and  $[\text{Cu}(6\text{-nitroquinoline})_2(\text{NCO})_2]$ , which are probably distorted tetrahedral complexes due to steric interactions encountered by the hydrogen atoms at the 8-positions of the quinoline molecules; and  $[\text{Cu}(\text{quinoline})(\text{NCO})_2]$ ,  $[\text{Ni}(4\text{-cyanopyridine})_2(\text{NCO})_2]$ , and  $[\text{Ni}(4\text{-carbomethoxyppyridine})_2(\text{NCO})_2]$ , which are postulated as being the first examples, along with  $\text{K}[\text{Cd}(\text{NCO})_3]$ , of complexes involving bridging cyanate groups. The latter complex appears to have a dimeric structure with four terminal N-bonded cyanates and two bridging cyanates, analogous to the structure suggested in the literature for  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Cd}_2(\text{NCSe})_6]$ .

### Introduction

Since the discovery<sup>2</sup> that the bonding mode adopted by the ambidentate thiocyanate ion is dependent upon the electronic character of the L ligand in square planar palladium(II) and platinum(II) com-

plexes of the type  $[\text{ML}_2(\text{thiocyanate})_2]$ , the existence of cooperative ligand effects, both electronic and/or steric in nature, involving the thiocyanate group has been demonstrated for a wide range of ligands and for octahedral metal complexes as well.<sup>3</sup> Although the bonding modes of the selenocyanate<sup>4</sup> and nitrite<sup>5</sup> ions have also been found to exhibit a sensitivity to steric effects of other ligands, the sensitivity of the bonding mode of the thiocyanate ion to changes in the electronic character of other ligands in the coordination sphere is unique. Comparable studies of ligand effects in palladium(II) and/or platinum(II) complexes of the nitrite,<sup>5</sup> selenocyanate,<sup>6</sup> and cyanate<sup>7</sup> ions have shown the bonding modes of these ligands to be insensitive to such changes, being, respectively, N-, Se- and N-bonded in all of the complexes examined.

The thiocyanate and selenocyanate ions are electronically analogous, in that both contain hard and soft atoms<sup>8</sup> which are capable of coordination, and their Group VI atom is the better  $\pi$ -acceptor site, by virtue of its vacant d orbitals and the fact that the largest lobes of the vacant  $\pi^*$  ligand orbitals are found on these less electronegative atoms. However, the nitrite and cyanate ions both contain two coordination sites which are generally classified as being hard, no lowlying vacant d orbitals are available on either atom, and the larger lobes of the vacant  $\pi^*$  ligand orbitals are found on the nitrogen atoms, thus rendering it a somewhat softer site than oxygen. The electronic cooperative ligand effects observed for the thiocyanate ion generally involve, at least in square planar complexes of palladium(II) and

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Table I. Preparative Methods, Colors, Decomposition Temperatures and Analytical Data for the Copper(II) Complexes

| L  | Preparative Method | Color     | Decomposition Temperature, °C | Analyses, %           |                  |                |                  |
|--|--------------------|-----------|-------------------------------|-----------------------|------------------|----------------|------------------|
|  |                    |           |                               | Cu                    | C                | H              | N                |
| [CuL <sub>2</sub> (NCO) <sub>2</sub> ] Complexes |                    |           |                               |                       |                  |                |                  |
| pyridine   | A                  | blue      | 113                           | 20.78<br>(20.93)      | 47.14<br>(47.31) | 3.30<br>(3.27) | 18.32<br>(18.47) |
| 4-methylpyridine                                 | A                  | blue      | 152                           | 19.03<br>(19.02)      | 50.37<br>(50.53) | 4.83<br>(4.65) | 16.78<br>(16.92) |
| 4-aminopyridine                                  | B                  | blue      | 175                           | 18.92<br>(18.61)      | 42.92<br>(42.74) | 3.60<br>(3.50) | 25.03<br>(24.91) |
| 4-acetylpyridine                                 | B                  | blue      | 151                           | 16.30<br>(16.19)      | 49.30<br>(49.11) | 3.62<br>(3.67) | 14.37<br>(14.54) |
| 4-carbomethoxypyridine                           | B                  | blue      | 159                           | 15.06<br>(15.11)      | 45.56<br>(45.75) | 3.35<br>(3.36) | 13.28<br>(13.42) |
| 4-cyanopyridine                                  | B                  | blue      | 132                           | 17.86<br>(17.41)      | 47.26<br>(47.32) | 2.27<br>(2.34) | 23.62<br>(23.47) |
| i-nicotinamide                                   | A                  | blue      | 187                           | 16.22<br>(16.11)      | 42.91<br>(43.11) | 3.09<br>(3.28) | 21.45<br>(21.28) |
| 4-pyridinealdoxime                               | B                  | green     | 97                            | 16.22<br>(16.45)      | 42.91<br>(42.75) | 3.09<br>(3.27) | 21.45<br>(21.23) |
| (2,2'-bipyridine) <sub>0.5</sub>                 | C                  | blue      | 213                           | 20.92<br>(21.05)      | 47.45<br>(47.30) | 2.65<br>(2.68) | 18.45<br>(18.30) |
| (1,10-phenanthroline) <sub>0.5</sub>             | C                  | blue      | 224                           | 19.39<br>(18.90)      | 51.31<br>(51.47) | 2.46<br>(2.62) | 17.09<br>(17.00) |
| i-quinoline                                      | B                  | blue      | 186                           | 15.66<br>(15.62)      | 59.19<br>(59.32) | 3.48<br>(3.46) | 13.80<br>(13.99) |
| (quinoline) <sub>0.5</sub>                       | D                  | green     | 145                           | 24.10<br>(23.68)      | 47.75<br>(47.63) | 2.55<br>(2.66) | 15.19<br>(15.01) |
| quinoline  | D                  | navy blue | 124                           | 15.66<br>(15.85)      | 59.19<br>(59.03) | 3.48<br>(3.54) | 13.80<br>(13.93) |
| 6-nitroquinoline                                 | B                  | blue      | 220                           | 12.81<br><sup>a</sup> | 48.45<br>(48.58) | 2.44<br>(2.53) | 16.95<br>(16.83) |
| [CuL <sub>2</sub> Cl <sub>2</sub> ] Complexes    |                    |           |                               |                       |                  |                |                  |
| 4-pyridinealdoxime                               |                    | green     | 208                           |                       | 38.06<br>(37.99) | 3.19<br>(3.35) | 14.79<br>(14.63) |
| 5-nitro-i-quinoline                              |                    | green     | 270                           |                       | 44.78<br>(44.83) | 2.51<br>(2.50) | 11.61<br>(11.42) |
| 5-nitroquinoline                                 |                    | green     | 208                           |                       | 44.78<br>(44.90) | 2.51<br>(2.60) | 11.61<br>(11.72) |
| 6-nitroquinoline                                 |                    | green     | 212                           |                       | 44.78<br>(44.64) | 2.51<br>(2.33) | 11.61<br>(11.51) |

<sup>a</sup> Could not be determined by analytical method employed

platinum(II), a S→N (soft→hard) bonding reversal upon the introduction of ligands which are good π-acceptors, e.g., triphenylphosphine. In view of the foregoing, it would seem more reasonable to search for a comparable N→O bonding reversal in nitrite or cyanate complexes of borderline or hard metal ions, e.g., copper(II) and nickel(II). This paper reports the results of such a study involving the cyanate ion.

## Experimental Section

**Preparation of Complexes.** [CuL<sub>2</sub>(NCO)<sub>2</sub>] Complexes. The following general method of preparation, with the indicated modifications, was employed:

(A) Copper(II) nitrate trihydrate (9.7 g., 40 mmol) was dissolved in 100 ml of water. A solution of 6.5 g (80 mmol) of potassium cyanate dissolved in 100 ml of water was added and, to the resulting blue solution, was immediately added a solution of 80

mmol of the ligand, dissolved in 50-100 ml of water. The precipitate which formed was isolated by filtration, washed with water, ethanol, and ether, and dried *in vacuo*.

(B) Same method, except that the ligand was dissolved in 100-200 ml of ethanol (200 ml of acetone for 6-nitroquinoline). The 4-acetylpyridine and 4-pyridinealdoxime complexes were not washed.

(C) Same method, except that 36 mmol of ligand, dissolved in 100 ml of ethanol, was used.

(D) The blue quinoline complex, [CuQ<sub>2</sub>(NCO)<sub>2</sub>], was prepared as described in (B), except that it was not washed. Washing the complex with ethanol yields the green [CuQ(NCO)<sub>2</sub>] complex. Reslurrying the latter in ethanol and adding quinoline results in the reappearance of the blue complex.

The compounds prepared are listed in Table I, along with their colors, decomposition temperatures, analyses, and references to the preparative method employed. The pyridine and 4-methylpyridine com-

**Table II.** Colors, Decomposition Temperatures, and Analytical Data for the  $[\text{NiL}_n(\text{NCO})_2]$  Complexes

| $L_n$  | Color  | Decomposition Temperature, °C | Analyses, %      |                  |                |                  |
|--|--------|-------------------------------|------------------|------------------|----------------|------------------|
|  |        |                               | Ni               | C                | H              | N                |
| (pyridine) <sub>4</sub>                            | blue   | 107                           | 12.79<br>(13.06) | 57.55<br>(57.45) | 4.39<br>(4.57) | 18.30<br>(18.46) |
| (4-methylpyridine) <sub>4</sub>                    | blue   | 137                           | 11.39<br>(11.24) | 60.61<br>(60.57) | 5.48<br>(5.61) | 16.31<br>(16.15) |
| (i-quinoline) <sub>4</sub>                         | blue   | 170                           | 8.90<br>(8.43)   | 69.22<br>(69.08) | 4.28<br>(4.23) | 12.75<br>(12.88) |
| (4-cyanopyridine) <sub>2</sub>                     | green  | 195                           | 16.73<br>(16.62) | 47.91<br>(47.79) | 2.30<br>(2.43) | 23.95<br>(23.85) |
| (4-carbomethoxypyridine) <sub>2</sub>              | green  | 198                           | 13.98<br>(14.00) | 46.08<br>(46.13) | 3.38<br>(3.49) | 13.43<br>(13.28) |
| (4-carbomethoxypyridine) <sub>2</sub> <sup>a</sup> | yellow | 230                           | 14.54<br>(14.43) | 41.63<br>(41.34) | 3.49<br>(3.54) | 6.94<br>(6.90)   |

<sup>a</sup> dichloro complex.

plexes have been reported previously,<sup>9,10</sup> albeit in a different context. Several attempts were made to prepare comparable copper(II) complexes containing triphenylphosphine, 5-nitro-1,10-phenanthroline, 5-nitroquinoline, and 5-nitro-i-quinoline, without success. In addition to method (B), a procedure was employed wherein a stoichiometric amount of the ligand was added to a solution of copper(II) cyanate in anhydrous methanol. In all cases, precipitates were isolated which did not yield satisfactory analytical results and could not be purified by recrystallization due to poor solubility in all solvents investigated.

**[CuL<sub>2</sub>Cl<sub>2</sub>] Complexes.** Each of the corresponding chloro compounds was also synthesized in order to assign the cyanate bands in the infrared spectra of the  $[\text{CuL}_2(\text{NCO})_2]$  complexes by comparing their spectra with those of the chloro derivatives. The general method of preparation consisted of dissolving 1.7 g (10 mmol) of copper(II) chloride dihydrate in absolute ethanol and slowly adding a solution of 20 mmol of the ligand (9 mmol for the bidentate ligands and the  $[\text{Cu}(\text{quinoline})\text{Cl}_2]$  complex, 10 mmol for 4-aminopyridine) in 100-200 ml of ethanol. The complex which precipitated was isolated by filtration, washed with ethanol and ether, and dried *in vacuo*. The 4-pyridinealdoxime complex was not washed, and the 6-nitroquinoline was dissolved in 200 ml of acetone. All of the complexes are green in color, with the exception of the 4-aminopyridine derivative (yellow),  $[\text{Cu}(\text{quinoline})\text{Cl}_2]$  (gold), and  $[\text{Cu}(\text{quinoline})_2\text{Cl}_2]$  (grey). Satisfactory C, H, and N analytical results were obtained for all of the complexes, but, since the majority have already been reported in the literature,<sup>11-19</sup> only the results for the new complexes are included in Table I.

**$[\text{NiL}_n(\text{NCO})_2]$  Complexes.** Except for the 4-carbomethoxypyridine derivative, the nickel(II) cyanate complexes shown in Table II were prepared by adding 6.4 g (80 mmol) of potassium cyanate, dissolved in 100 ml of water, to a solution of 11.6 g (40 mmol) of nickel(II) nitrate hexahydrate dissolved in 100 ml of water. To the resulting blue solution was added 180 mmol of ligand, dissolved in 100 ml of ethanol (200 ml of 50% (v/v) ethanol-acetone, in the case of 4-cyanopyridine). The resulting precipitate was isolated by filtration, washed with ethanol and ether, and air dried. In the case of the 4-methylpyridine and i-quinoline derivatives, the ligand, dissolved in 100 ml of ethanol, was added to the nickel(II) nitrate solution prior to the addition of the potassium cyanate solution. The pyridine, 4-methylpyridine, and i-quinoline complexes have previously been reported in the literature.<sup>20</sup> The 4-carbomethoxypyridine derivative was prepared by a method analogous to that given by Nelson and Shepherd<sup>21</sup> for the preparation of  $[\text{Ni}(\text{pyridine})_4\text{Cl}_2]$ .

**$[\text{NiL}_n\text{Cl}_2]$  Complexes.** The pyridine, 4-methylpyridine, and i-quinoline complexes were prepared according to the method of Nelson and Shepherd.<sup>21</sup> The 4-cyanopyridine and 4-carbomethoxypyridine derivatives were prepared by adding a solution of nickel(II) chloride hexahydrate (9.5 g, 40 mmol) dissolved in 50 ml of ethanol to a solution of excess ligand dissolved in 100 ml of ethanol. The precipitate which formed was isolated by filtration, washed with ethanol and ether and dried *in vacuo*. The  $[\text{NiL}_4\text{Cl}_2]$  complexes are blue (pyridine, 4-methylpyridine) or green (i-quinoline) in color, whereas the  $[\text{NiL}_2\text{Cl}_2]$  complexes are yellow. The analytical data for the new 4-carbomethoxypyridine complex are shown in Table II.

**$[\text{Ni}(1,10\text{-phenanthroline})_2(\text{NCO})_2]$ .** Dicyanato-N-tetrapyridinenickel(II) (2.3 g, 5 mmol) was placed in a 250 ml round bottom flask equipped with a stir-

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Table III. Solid State Infrared Spectra for  $[ML_n(NCO)_2]$  Complexes ( $cm^{-1}$ )

| Complex                               | $\nu_{CN}$        | $\nu_{CO}$       | $\delta_{NCO}$            |
|---------------------------------------|-------------------|------------------|---------------------------|
| $[CuL_2(NCO)_2]$ , L =                |                   |                  |                           |
| pyridine                              | 2208              | 1320             | 625, 611                  |
| 4-methylpyridine                      | 2221              | 1345             | 617                       |
| 4-aminopyridine                       | 2243              | 1320             | 608                       |
| 4-acetylpyridine                      | 2221              | 1330             | 619                       |
| 4-carbomethoxypyridine                | 2217              | <sup>a</sup>     | 631, 619                  |
| 4-cyanopyridine                       | 2232 <sup>b</sup> | 1350             | 632, 614                  |
| i-nicotinamide                        | 2212, 2201        | 1335             | 625, 617, 608             |
| 4-pyridinealdoxime                    | 2221              | 1330             | 618                       |
| (2,2'-bipyridine) <sub>0.5</sub>      | 2211, 2189        | 1340             | 630, 619                  |
| (1,10-phenanthroline) <sub>0.5</sub>  | 2236, 2189        | 1322, 1310       | 617, 606                  |
| i-quinoline                           | 2209              | 1335             | 628, 617                  |
| (quinoline) <sub>0.5</sub>            | 2207, 2165        | 1360, 1330       | 689, 668, 617             |
| quinoline                             | 2220, 2190        | 1335             | 655, 625, 615, 603        |
| 6-nitroquinoline                      | 2235, 2222        | <sup>a</sup>     | 639, 610                  |
| $R_2[Cu(NCO)_4]$ <sup>c</sup>         | 2247, 2183        | 1328             | 619, 617, 612             |
| KNCO <sup>d</sup>                     | 2165              | 1302, 1207       | 637, 628                  |
| $[NiL_n(NCO)_2]$ , L <sub>n</sub> =   |                   |                  |                           |
| (pyridine) <sub>4</sub>               | 2207              | 1315             | 615, 620                  |
| (4-methylpyridine) <sub>4</sub>       | 2202              | 1320, 1312, 1305 | 618                       |
| (i-quinoline) <sub>4</sub>            | 2193              | 1320             | 620                       |
| (4-cyanopyridine) <sub>2</sub>        | 2188 <sup>e</sup> | 1308             | 680 sh, 665, sh, 620, 600 |
| (4-carbomethoxypyridine) <sub>2</sub> | 2240, 2192, 2125  | 1300             | 695, 675, 625, 600        |
| (1,10-phenanthroline) <sub>2</sub>    | 2200, 2165        | 1300             | 627, 621, 610             |
| $R_2[Ni(NCO)_4]$ <sup>c</sup>         | 2237, 2186        | 1330             | 619, 617                  |
| $[Zn(pyridine)_2(NCO)_2]$             | 2230              | 1355             | 622                       |
| $[Cd(pyridine)_2(NCO)_2]$             | 2180              | 1352             | 654, 633                  |
| $K[Cd(NCO)_3]$                        | 2250, 2202        | 1348             | 660, 647, 625, 620        |
| $R_2[Cd(NCO)_4]$ <sup>c</sup>         | 2262, 2174        | 1328             | 621                       |

<sup>a</sup> Region obscured by ligand absorption. <sup>b</sup> Masks  $\nu_{CN}$  of nitrile expected at  $2240\text{ cm}^{-1}$ . <sup>c</sup> R =  $(C_2H_5)_4N^+$ , data taken from ref. 38. <sup>d</sup> Data taken from A. Maki and J. C. Decius, *J. Chem. Phys.*, 31, 772 (1959). <sup>e</sup> Nitrile  $\nu_{CN}$  at  $2242\text{ cm}^{-1}$ .

ring bar and reflux condenser. With continuous purging with dry nitrogen, 100 ml of pyridine was added and the suspension stirred for 1.5 hr. The suspension was then heated at reflux for 1 hr, whereupon most of the complex dissolved. A solution of 1.8 g (10 mmol) of 1,10-phenanthroline in 50 ml of pyridine was added slowly to the flask, yielding a green solution. The mixture was stirred for 0.5 hr, and then allowed to cool to room temperature. The blue-green precipitate which formed was isolated by filtration, suction dried on the filter, and dried *in vacuo*. Decomposition temperature  $298^\circ\text{C}$ . This procedure parallels that used by Schilt and Fritsch<sup>22</sup> to prepare the corresponding thiocyanate complex.

*Anal.* Calcd. for  $C_{26}H_{16}N_6NiO_2$ : C, 62.06; H, 3.21; N, 16.70. Found: C, 61.94; H, 3.27; N, 16.93.

*Zinc(II) and Cadmium(II) Complexes.* The complexes  $[M(\text{pyridine})_2X_2]$  (M =  $Zn^{II}$ ,  $Cd^{II}$ ; X =  $-NCO^-$ ,  $Cl^-$ ) were prepared according to methods given in the literature.<sup>11,20,23</sup> The complex first prepared and formulated by Ripan<sup>24</sup> as  $K[Cd(NCO)_3]$  was synthesized by adding a solution of 13.0 g (160 mmol) of potassium cyanate dissolved in 50 ml of water to a solution of 12.3 g (40 mmol) of cadmium(II) nitrate tetrahydrate dissolved in 100 ml of water. The white precipitate which formed was isolated by filtration, washed with ethanol and ether, and dried *in vacuo*.

*Anal.* Calcd. for  $C_3CdKN_3O_3$ : C, 12.98; H, 0.00; N, 15.14; Cd, 40.50. Found: C, 12.86; H, 0.13; N, 15.16; Cd, 40.93.

*Analyses.* Carbon, hydrogen, and nitrogen analyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, Germany and the M-H-W Laboratories, Garden City, Michigan. Percent copper was determined<sup>25</sup> using the potassium iodide-sodium thiosulfate method. After destroying the complex by either ashing or perchloric acid digestion, the copper was dissolved, excess acid neutralized, and the solution analyzed as described in the reference. The thiosulfate and iodide solutions were standardized against electrolytic copper. Percent nickel was determined by the potassium cyanide-silver nitrate method.<sup>26</sup> Nickel solutions were prepared from the complexes in the same manner as described for copper. Percent cadmium was determined<sup>27</sup> by forming the « oxime » complex,  $Cd(C_9H_6ON)_2$ , which was dried and weighed.

*Infrared Spectra.* Survey spectra were measured with a Perkin Elmer Model 337 double beam grating spectrophotometer in the range  $4000\text{--}400\text{ cm}^{-1}$ , using either Nujol mulls between KBr plates or pressed KBr disks. A Perkin Elmer Model 421 double beam grating spectrophotometer was also used both for recording survey spectra and, in a four-fold wave number scale expansion, for precise measurement of

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**Table IV.** Molar Conductance and Electronic Spectral Data for the  $[\text{CuL}_2(\text{NCO})_2]$  Complexes

| L                                    | N,N-dimethylformamide  |                            |  | Acetonitrile   |                            |  |
|--------------------------------------|--|----------------------------|--|--|----------------------------|--|
|                                      | $\Lambda_m,^a$<br>ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> | $\nu_{\text{max}}$ ,<br>kK | $\epsilon$ ,<br>M <sup>-1</sup> cm <sup>-1</sup> | $\Lambda_m,^a$<br>ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> | $\nu_{\text{max}}$ ,<br>kK | $\epsilon$ ,<br>M <sup>-1</sup> cm <sup>-1</sup> |
| pyridine                             | 41   | 12.5                       | 32   | 16   | 14.5                       | 95   |
| 4-methylpyridine                     | 41   | 12.5                       | 37   | 12   | 14.5                       | 88   |
| 4-aminopyridine                      | 48   | 12.5                       | 42   | b  | b                          | b  |
| 4-acetylpyridine                     | 33   | 12.5                       | 46   | 37   | 13.5                       | 79   |
| 4-carbomethoxypyridine               | 47   | 12.5                       | 29   | 25   | 14.0                       | 82   |
| 4-cyanopyridine                      | 48   | 12.5                       | 34   | 25   | 13.5                       | 88   |
| i-nicotinamide                       | 38   | 12.5                       | 37   | b  | b                          | b  |
| (2,2'-bipyridine) <sub>0.5</sub>     | 28   | 15.5                       | 93   | b  | b                          | b  |
| (1,10-phenanthroline) <sub>0.5</sub> | 7.5  | 15.0                       | 74   | b  | b                          | b  |
| i-quinoline                          | 41   | 12.5                       | 33   | b  | b                          | b  |
| (quinoline) <sub>0.5</sub>           | 21   | 12.8                       | 73   | b  | b                          | b  |
| quinoline                            | 27   | 12.8                       | 71   | b  | b                          | b  |
| 6-nitroquinoline                     | 30   | 12.5                       | 45   | b  | b                          | b  |

<sup>a</sup> Observed  $\Lambda_m$  values for  $10^{-3} M$  solutions at 25°: DMF: non-electrolytes, 7-42; 1:1 electrolytes, ca. 85 (ref. 43); acetonitrile: 1:1 electrolytes, ca. 170 [J. L. Burmeister, S. D. Patterson, and E. A. Deardorff, *Inorg. Chim. Acta*, 3, 105 (1969)]; nitromethane: non-electrolytes, 10-13; 1:1 electrolytes, 80-90 (ref. 35). <sup>b</sup> Insufficient solubility for measurement.

$\nu_{\text{CN}}$  bands. The  $\nu_{\text{CN}}$ ,  $\nu_{\text{CO}}$  and  $\delta\text{NCO}$  frequencies for the cyanate complexes are shown in Table III. The  $\nu_{\text{CN}}$  and  $\delta\text{NCO}$  frequencies were determined from Nujol mull spectra, whereas those of the  $\nu_{\text{CO}}$  bands were determined from KBr disk spectra, due to partial masking of the  $\nu_{\text{CO}}$  region by a Nujol absorption band. No substitution of bromide for cyanate in the KBr disks was observed, as evidenced by the absence of an ionic  $\nu_{\text{CN}}$  band at 2165 cm<sup>-1</sup> in all of the KBr disk spectra. Band assignments were based on comparisons of the spectra of the cyanate complexes with those of the corresponding chloride complexes. The  $\nu_{\text{M-Cl}}$  bands present no complicating interference, since they occur<sup>11,28</sup> below 400 cm<sup>-1</sup>.

**Conductance Measurements.** Molar conductances, at 25°C, of  $10^{-3} M$  solutions of the complexes in various solvents were determined with an Industrial Instruments, Inc. Model RCI6B2 conductivity bridge and a cell with platinized electrodes. The  $\Lambda_m$  values for those copper(II) complexes which exhibited the necessary solubility are shown in Table IV. The  $\Lambda_m$  values for nitromethane solutions of the  $[\text{NiL}_2(\text{NCO})_2]$  complexes, where L = pyridine, 4-methylpyridine, and (1,10-phenanthroline)<sub>0.5</sub>, were found to be, respectively, 2.5, 4.5, and 7.0 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>.

**Ultraviolet, Visible, and Near Infrared Spectra.** Solution spectra were measured with a Cary Model 14 double beam prism spectrophotometer from 1200 to 300 nm, using matched 1.01 cm quartz cells. The absorption maxima found in the spectra of the copper(II) complexes which exhibited adequate solubility are shown in Table IV. Attempts were made to obtain solid state VIS-UV absorption spectra of the highly insoluble nickel(II) complexes held in Nujol suspension between quartz plates, using Nujol-impregnated filter paper as a scattering agent in both the sample and reference beams, but the absorption bands were too weak to be distinguished from the background noise.

(28) D. A. Adams, *Metal-Ligand and Related Vibrations*, St. Martin's Press, New York, N. Y., 1968, chap. 2.

## Discussion

**Cyanate Bonding Mode.** Although the cyanate ion has shown a marked preference for coordination through the nitrogen atom,<sup>29</sup> a few O-bonded complexes have been reported quite recently.<sup>30,31</sup> It is now reasonably certain that the frequency and/or integrated absorption intensity<sup>30</sup> of the cyanate  $\nu_{\text{CN}}$  band cannot be used to assign the bonding mode of the coordinated cyanate group unambiguously. However, the  $\nu_{\text{CX}}$  (X = O, S, Se) bands of the cyanate, thiocyanate, and selenocyanate ions have been found to behave<sup>3,29,30,31</sup> in a parallel manner, increasing in frequency upon N-coordination and decreasing in frequency upon X-coordination. The  $\delta\text{NCO}$  bending frequency is also of some diagnostic value, generally being higher (above 600 cm<sup>-1</sup>) for N-coordinated complexes.

Copper(II) was chosen as the coordination site for initial investigation in this study because it is prone to form square planar complexes, as does palladium(II) and platinum(II), and the results of this study could then be correlated with those of the extensive previous studies with NCO<sup>-</sup>, NCS<sup>-</sup>, and NCS<sup>-</sup> in square planar systems.<sup>3,6,7</sup> It also is generally classified as being on the borderline between hard and soft Lewis acid behavior. Nickel(II) was included in the study because, in addition to forming square planar complexes and being a hard metal ion, it frequently assumes coordination number six. The ligands employed represent a compromise between theoretical desirability and synthetic feasibility. Complexes containing typical  $\pi$ -acceptor ligands such as phosphines and arsines could not be synthesized. However, the aromatic amines utilized all possess vacant  $\pi^*$  orbitals and, hence, a potential  $\pi$ -acceptor function. Indeed, the reaction<sup>32</sup> between  $[\text{Pd}(\text{SCN})_4]^{2-}$  and 2,2'-bipyridine yields an N-bonded

(29) See references cited in J. L. Burmeister and N. J. De Stefano, *Inorg. Chem.*, 8, 1546 (1969).

(30) J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *Inorg. Chem.*, 8, 170 (1969).

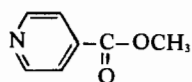
(31) R. A. Bailey and S. L. Kozak, *J. Inorg. Nucl. Chem.*, 31, 689 (1969).

(32) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 3, 1587 (1964).

species,  $[\text{Pd}(\text{bipy})(\text{NCS})_2]$ , as the stable isomer, to cite only one of several<sup>3</sup> comparable examples.

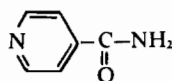
Nonetheless, it is quite clear from the infrared data shown in Table III, especially the increased (relative to the free ion)  $\nu\text{CO}$  frequency values, that, with the possible exception of four bridged complexes (which will be discussed later), all of the cyanate groups in the complexes are N-bonded. This is, perhaps, not too surprising in view of the metal ions  $[\text{Ti}^{\text{IV}}, \text{Zr}^{\text{IV}}, \text{Re}^{\text{IV}}, \text{Re}^{\text{V}}, \text{and Mo}^{\text{III}}]$  which have now been found<sup>30,31</sup> to coordinate to the oxygen atom of the cyanate. All have either vacant or only partially filled  $d_\pi$  orbitals which have the appropriate symmetry to interact with the filled  $\pi$ -bonding orbitals of the cyanate, the largest lobes of which are found on the most electronegative oxygen atom. With such high oxidation states, the tendency for electron donation by the metal would be slight, and electron acceptance would tend to counterbalance the high positive charge on the metal. The removal of enough electron density from the  $d_\pi$  orbitals of either copper(II) or nickel(II) to cause them to switch from bonding to the nitrogen atom *via* a bond involving (in addition to the sigma component)  $d_\pi(\text{metal}) \rightarrow \pi^*(\text{ligand})$  interaction to bonding to the oxygen atom *via* a bond involving  $\pi(\text{ligand}) \rightarrow d_\pi(\text{metal})$  interaction undoubtedly will require the presence of ligands having a much stronger  $\pi$ -acceptor capacity, assuming that such a complex can be made. It is more probable that cooperative ligand effects of this type will be operable in cyanate complexes of metal ions which are less electron-rich in their  $d_\pi$  orbitals.

**Structure of the Complexes.** Although the VIS-UV spectra of the copper(II) cyanate complexes were measured, the values of the absorption maxima (Table IV) are not indicative of the electronic environment in the solid state, since the complexes change color from blue to yellow-green upon dissolution. This is most probably due to coordination of solvent molecules above and below the square plane rather than dissociation of the complex, since the results of the conductivity measurements (Table IV) indicate that dissociation of the complexes is very slight, especially in acetonitrile.

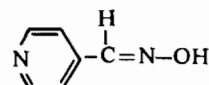


4-carbomethoxypyridine

The copper(II) pyridine, 4-methylpyridine, 4-aminopyridine, 4-acetylpyridine, 4-carbomethoxypyridine, 4-cyanopyridine and i-quinoline cyanate complexes are assigned a *trans* square planar structure because the  $\nu\text{CN}$  band is a singlet (only the out-of-phase CN stretching frequency would be infrared active). The 2,2'-bipyridine and 1,10-phenanthroline complexes are undoubtedly *cis* square planar, and exhibit the expected  $\nu\text{CN}$  doublet in their infrared spectra (the inphase CN stretching mode also being infrared active in the *cis* structure).



i-nicotinamide



4-pyridinealdoxime

The remaining copper(II) cyanate complexes present some structural anomalies, the least understood of which is the splitting of the  $\nu\text{CN}$  mode of the i-nicotinamide complex. This could be indicative of a *cis* structure, but is more probably due to a solid state splitting effect. Since the other copper(II) complexes discussed above are blue, the green 4-pyridinealdoxime complex is probably in an octahedral environment created by bridging by the aldoxime substituent. Further evidence in support of a bridged polymeric species is the insolubility of the complex in DMF, whereas all of the other derivatives are soluble. The cyanate frequencies exhibited by the complex are all normal, and give no indication of cyanate bridging.

The quinoline ligand provides the most interesting structural variations, in that two quinoline complexes are formed,  $[\text{CuQ}(\text{NCO})_2]$  and  $[\text{CuQ}_2(\text{NCO})_2]$ . The former is the more stable, *i.e.*, simply washing the solid blue bis(quinoline) complex with alcohol, acetone, or dichloromethane immediately converts it to the green solid monoquinoline complex. The split  $\nu\text{CN}$  band (Table III) and intense blue color exhibited by the bis(quinoline) complex, could result from either a tetrahedral or *cis*-square planar structure with the quinoline molecules tilted out of the plane. Although its energy level scheme is admittedly quite different, it should be noted that the intense blue isomer of the  $[\text{NiQ}_2\text{Cl}_2]$  complex is tetrahedral.<sup>33</sup> The green monoquinoline complex could either be 3-coordinate or a bridged species with the quinoline bent out of the square plane to relieve strain. Some evidence in support of the latter possibility is seen in the slow rate of dissolution of the complex in DMF when compared with the other copper(II) cyanate complexes (2 days *vs.* a few minutes) and the high frequency  $\delta\text{NCO}$  bands (*vide infra*). Upon dissolving the blue  $[\text{CuQ}_2(\text{NCO})_2]$  complex in DMF, a green solution is formed, the visible spectrum of which is essentially identical (Table IV) to that of a DMF solution of  $[\text{CuQ}(\text{NCO})_2]$ . Not enough evidence is available to assign definite structures to either of these complexes. It is significant that i-quinoline, which would be expected to experience less steric interactions, forms only the normal  $[\text{Cu}(i\text{-Q})_2(\text{NCO})_2]$  complex.

Copper(II) chloride complexes having stoichiometries analogous to those of the cyanate complexes were prepared for all of the ligands except 4-aminopyridine, for which only the complex  $[\text{Cu}(4\text{-aminopyridine})\text{Cl}_2]$  could be isolated. This complex probably contains bridging pyridine-amine groups. The pyridine complex  $[\text{Cu}(\text{py})_2\text{Cl}_2]$  has been shown<sup>13</sup> to be octahedral with bridging chlorides. However, Goldstein, *et al.*,<sup>17</sup> have shown that substituted pyridine complexes and quinoline complexes of  $\text{CuCl}_2$

(33) D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963).

do not have bridging chlorides and therefore must involve square planar copper(II).

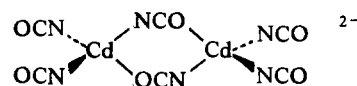
The  $[\text{NiL}_4(\text{NCO})_2]$  complexes also exhibit some interesting structural variations. The singlet  $\nu\text{CN}$  bands for the pyridine, 4-methylpyridine, and *i*-quinoline complexes suggest *trans* octahedral structures. The doublet  $\nu\text{CN}$  bands for the 1,10-phenanthroline derivative, however, suggests a *cis* octahedral arrangement. This coordination behavior parallels that observed for the corresponding thiocyanate complexes, *i.e.*,  $[\text{Ni}(\text{py})_4(\text{NCS})_2]$  has been shown<sup>34</sup> to have a *trans* structure, whereas  $[\text{Ni}(\text{phen})_2(\text{NCS})_2]$  is believed to have a *cis* structure.<sup>22,35</sup> The reason for the *cis* structure in the case of the 1,10-phenanthroline complexes becomes apparent when they are compared with the structure of the *trans*- $[\text{Ni}(\text{py})_4(\text{NO}_2)_2]$  complex, wherein the pyridine nitrogen atoms are coplanar with the nickel atom, but the pyridine rings are tilted with respect to this plane,<sup>36</sup> evidently because of steric interactions between the alpha hydrogens on adjacent pyridines. In the case of 1,10-phenanthroline, such tilting cannot take place, and the molecule is forced into a *cis* configuration. Solubility considerations prohibited the measurement of solution VIS-UV spectra for the nickel(II) cyanate complexes.

The 4-cyanopyridine and 4-carbomethoxypyridine nickel(II) complexes precipitate as the bis complexes, even in the presence of excess ligand. Their pale green color, coupled with extinction coefficients so low that their absorption maxima could not be distinguished from the background noise in their Nujol mull VIS-UV spectra, argue against their having square planar or tetrahedral structures. For example, tetrahedral  $[\text{Ni}(\text{quinoline})_2\text{Cl}_2]$  is intense blue in color, as mentioned earlier, while its pale yellow isomer is bridged octahedral.<sup>33</sup>

If, as indicated by their color and low solubility, the structures of the 4-cyanopyridine and 4-carbomethoxypyridine complexes do involve bridging groups, the question arises as to which of the coordinated groups is doing the bridging. In the free 4-cyanopyridine, the nitrile  $\nu\text{CN}$  band occurs at  $2240\text{ cm}^{-1}$ . It has been shown by Farha and Iwamoto<sup>37</sup> that coordination *via* the nitrogen atom of the pyridine ring does not affect the  $\nu\text{CN}$  frequency of the nitrile group, whereas nitrile coordination results in an increase of 5 to  $25\text{ cm}^{-1}$ . Since the nitrile  $\nu\text{CN}$  band of the complex is found at  $2242\text{ cm}^{-1}$ , it would appear that the nitrile group is not involved in bridging. Likewise, since the frequency of the  $\nu\text{CO}$  band of the 4-carbomethoxypyridine ligand is not shifted upon coordination, the ester group also would not appear to be involved in bridging. This suggests cyanate bridging in both cases.

In an effort to study an authentic complex containing bridging cyanate groups, a complex formulated in the older literature<sup>24</sup> as  $\text{K}[\text{Cd}(\text{NCO})_3]$  was investigated. It was found that it precipitates from water

even in an excess of potassium cyanate, indicating that it has a more stable crystal structure than does  $\text{K}_2[\text{Cd}(\text{NCO})_4]$ . The  $[\text{Cd}(\text{NCO})_4]^{2-}$  complex ion can be prepared as the  $[(\text{C}_2\text{H}_5)_4\text{N}]^+$  salt only in non-aqueous media<sup>38</sup> and has a completely different infrared spectrum (Table III). Several other compounds have been reported which have a formula in the solid state which is analogous to  $\text{K}[\text{Cd}(\text{NCO})_3]$ , among them being  $\text{Cs}[\text{CuCl}_3]$ , in which the geometry about the copper atom is square planar, being coordinated to four chlorides in long bridging chains;<sup>39</sup>  $\text{NH}_4[\text{HgCl}_3]$ , in which the mercury atom is six-coordinate and the  $\text{HgCl}_6$  octahedra are linked in layers;<sup>40</sup>  $\text{NH}_4[\text{CdCl}_3]$ , in which the cadmium is six-coordinate and the  $\text{CdCl}_6$  octahedra form double chains in one direction;<sup>41</sup> and  $[(\text{n-C}_4\text{H}_9)_4\text{N}][\text{Cd}(\text{NCSe})_3]$ , which is believed, on the basis of infrared evidence, to involve discrete  $[\text{Cd}_2(\text{NCSe})_6]^{2-}$  ions with two bridging selenocyanate groups.<sup>42</sup> It would therefore seem reasonable to predict that three-coordinate cadmium(II) is not present in  $\text{K}[\text{Cd}(\text{NCO})_3]$  but, instead, bridging cyanate groups are involved. Whether the anion is a dimer,  $[\text{Cd}_2(\text{NCO})_6]^{2-}$ , involving tetrahedral geometry about the cadmium(II),



as proposed for the  $[(\text{n-C}_4\text{H}_9)_4\text{N}][\text{Cd}_2(\text{NCSe})_6]$  complex,<sup>42</sup> or whether the  $\text{Cd}(\text{NCO})_3$  units link up to form a chain of octahedra is not certain. Some weight is given to the  $[\text{Cd}_2(\text{NCO})_6]^{2-}$  dimer structure since the splitting pattern of its  $\nu\text{CN}$ ,  $\nu\text{CO}$ , and  $\delta\text{NCO}$  bands is quite comparable to the splitting pattern of the corresponding bands in the infrared spectrum of the  $[\text{Cd}_2(\text{NCSe})_6]^{2-}$  complex.

The molar conductivity of the cyanate complex was measured in DMF. If calculated on the basis of the dimer,  $\text{K}_2[\text{Cd}_2(\text{NCO})_6]$ ,  $\Lambda_m = 122$ ; if calculated on the basis of the monomer,  $\text{K}[\text{Cd}(\text{NCO})_3]$ ,  $\Lambda_m = 61$ . Unfortunately, a distinction cannot be made between the two on this basis since 1:1 electrolytes generally exhibit  $\Lambda_m$  values of 85 or less and 2:1 electrolytes exhibit values between 140 and 170 for  $10^{-3}\text{ M}$  DMF solutions.<sup>43</sup> Furthermore, as the complex dissolves in DMF, a small amount of material reprecipitates, indicating that the species in solution is probably not the same as that in the solid state.

What is most striking, however, is the similarity in multiplicity and frequency among the  $\delta\text{NCO}$  bands exhibited by this complex and the other complexes which we have postulated as containing bridging cyanate groups:  $[\text{Cu}(\text{quinoline})(\text{NCO})_2]$ ,  $[\text{Ni}(4\text{-cyanopyridine})_2(\text{NCO})_2]$  and  $[\text{Ni}(4\text{-carbomethoxypyridine})_2(\text{NCO})_2]$ . Although bridging thiocyanate and selenocyanate groups are well known,<sup>3</sup> these complexes ap-

(34) M. A. Porai-Koshits, A. S. Antsishkina, L. M. Dickareva, and E. K. Jukhnov, *Acta Cryst.*, **10**, 784 (1957).

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(36) M. A. Porai-Koshits and A. S. Antsishkina, *Dokl. Akad. Nauk. SSSR*, **92**, 333 (1953).

(37) F. Farha, Jr. and R. T. Iwamoto, *Inorg. Chem.*, **4**, 844 (1965).

(38) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262 (1965).

(39) A. F. Wells, *J. Chem. Soc.*, 1662 (1947).

(40) E. J. Harmsen, *Z. Krist.*, **100**, 208 (1938).

(41) H. Brasseur and L. Pauling, *J. Am. Chem. Soc.*, **60**, 2886 (1938).

(42) J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, **5**, 1113 (1966).

(43) J. V. Quagliano, J. Fujita, G. Frantz, D. J. Phillips, J. A. Walsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).



parently represent the only examples of such bonding involving the cyanate group thus far reported.<sup>44</sup> This

(44) After this manuscript had been submitted for publication, Nelson and Nelson reported [*J. Chem. Soc.*, (A) 1597 (1969)] the synthesis and characterization of a series of six coordinate complexes of the type  $[ML_2(NCO)_3]$  ( $M = Mn, Fe, Co, \text{ or } Ni$ ;  $L = 3\text{- or } 4\text{-cyanopyridine}$ ), wherein the cyanate groups are believed to form bridges *via* their nitrogen atoms,  $M \begin{array}{c} \diagdown \\ N \\ \diagup \\ C \\ | \\ O \end{array} M$ . The infrared evidence presented by

these authors in support of this bonding mode is analogous to that observed in this study, and the same conclusion regarding the nature of the cyanate bridges in the  $[Cu(\text{quinoline})(NCO)_2]$ ,  $[Ni(4\text{-carboxy-pyridine})_2(NCO)_2]$ , and  $K_2[Cd_2(NCO)_6]$  complexes would appear to be applicable. This serves as a further illustration of the unique coordination behavior of the cyanate group, since the thiocyanate and selenocyanate ions are known to form bridges only of the type  $M\text{-NCX-M}$ .

is especially significant, since several reports have appeared in the literature<sup>20,45,46</sup> wherein the cyanate ion was observed to form only non-bridged complexes under circumstances which yielded only bridged complexes when other pseudohalide ions ( $NCS^-$ ,  $NCS_2^-$ ,  $N_3^-$  and/or  $CN^-$ ) were present.

**Acknowledgement.** The authors wish to express their appreciation for the support of this research by the National Science Foundation (Grant No. GP-8327).

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