



ساختار بلوری کمپلکس ترانس - [بیس (۵،۲-دی کلروفنیل سیانامیدو)  
{N',N} - پروپان دی ایل بیس (۲، ۳- بوتادیان ۲-ایمین - ۳- اکسیم)}  
کبالت (III) ]،  $trans-[Co((DO)(DOH)pn)(2,5-Cl_2pcyd)_2]$

حسن حدادزاده، علیرضا رضوانی

گروه شیمی، دانشگاه سیستان و بلوچستان، زاهدان، صندوق پستی: ۶۷۴ - ۹۸۱۳۵  
پست الکترونیکی: [hadad@hamoon.usb.ac.ir](mailto:hadad@hamoon.usb.ac.ir)

(دریافت مقاله ۱۳۸۲/۹/۲ ، دریافت نسخه نهایی ۱۳۸۳/۴/۱)

**چکیده:** اولین ساختار بلوری یک کمپلکس فنیل سیانامید کبالت اکسیم (کبال اکسیم) گزارش شده است. این کمپلکس با فرمول  $trans-[Co((DO)(DOH)pn)(2,5-Cl_2pcyd)_2]$  است که در آن یک لیگاند چهار دندانه‌ای ((DO)(DOH)pn) از نوع ایمین-اکسیم در موقعیت استوایی و دو لیگاند ۲، ۵-دی کلروفنیل سیانامید (2,5-Cl<sub>2</sub>pcyd) در موقعیت محوری قرار دارند. بلورهای کمپلکس  $trans-[Co((DO)(DOH)pn)(2,5-Cl_2pcyd)_2]$  توسط نفوذ اتر به داخل محلول استونیتریلی آن رشد داده شد. ساختار بلوری مربوط به این کمپلکس ارتورومبیک (گروه فضایی از نوع Pbc<sub>a</sub>) با پارامترهای شبکه‌ای  $a = 13,680$ ،  $b = 13,743$ ،  $c = 29,892$  آنگستروم،  $R = 0,0606$ ،  $I > 2\sigma(I)$  (۲۹۴۶) و  $Z = 8$  هر دو لیگاند ۲، ۵-دی کلروفنیل سیانامید از سمت نیتروژن عامل نیتریلی به کبالت (III) کوئوردینه شده‌اند. زاویه پیوندی کبالت (III)-سیانامید (Co(III)-N=C=N-ph) خمیده است ولی گروه سیانامید (-N=C=N-) با حلقه فنیل در یک صفحه قرار دارد. این ساختار هندسی ناشی از اهمیت نسبی برهم‌کنش  $\pi$  در این پیوند است.

واژه‌های کلیدی: اکسیم، ایمین، کمپلکس کبالت (III)، فنیل سیانامید، شبه هالیدها، ویتامین B<sub>12</sub>.

**Crystal Structure of *Trans*-  
[bis(2,5-dichlorophenylcyanamido)  
{N,N'-propanediylbis(2,3-butadien-2-imine-3-oxime)}  
Cobalt(III)], *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>]**

**H. Hadadzadeh, A.R. Rezvani**

*Chemistry Department, Sistan & Baluchestan University, Zahedan, P.b.: 98135-674.  
E-mail: hadad@hamoon.usb.ac.ir.*

(received: 23/11/2003, received in revised form: 22/06/2004)

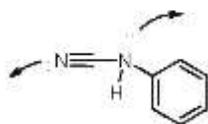
**Abstract:** The first crystal structure of a phenylcyanamide cobaltoxime (cobaloxime) complex is reported. This compound is *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>], and consists of an imine-oxime equatorial ligand ((DO)(DOH)pn) and two 2,5-dichlorophenylcyanamide ligands in axial positions. Crystals of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] were grown by ether diffusion into an acetonitrile solution of the complex. Crystal structure of this complex is orthorhombic (space group: Pbc<sub>a</sub>) with  $a = 13.6800$ ,  $b = 13.7434$ ,  $c = 29.892$  Å, and  $Z = 8$ . The structure was refined by using 2946 independent reflections with  $I > 2\sigma(I)$  to a R factor of 0.0606. Both phenylcyanamide ligands are coordinated to Co(III) through the terminal nitrile nitrogen of the cyanamide group. In addition, the cobalt(III)-cyanamide (Co(III)-N=C=N-ph) bond angle is significantly bent while the cyanamide group (N=C=N-) is largely coplanar with the phenyl ring. These geometries can be ascribed to the relative importance of  $\pi$  bonding.

**Keywords:** *Oxime, Imine, Phenylcyanamide, Cobalt(III) Complex, Vitamin B<sub>12</sub>, Pseudohalides.*

### Introduction

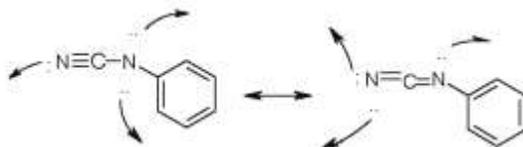
The coordination chemistry of cobaloximes and cobaloxime-imines has been studied extensively in recent years with emphasis on the role of axial ligands on electrochemical and photochemical behavior and in particular on the use of these systems as models of vitamin B<sub>12</sub> [1 - 9].

Phenylcyanamide coordination chemistry has been the subject of a recent review [10]. Phenylcyanamide ligands (pcyd) are pseudohalides like azide or thiocyanate [11]. However, the attachment of phenyl ring to the cyanamide group (-N=C=N) adds an extra dimension which is not present in azide or thiocyanate ligands. An extensive  $\pi$  conjugation between the cyanamide group and the phenyl ring provides an energetically favorable means by which a metal ion can couple into a conjugated organic  $\pi$  system. The phenylcyanamides are ambidentate ligands whether neutral or in anionic form and so the possibility of linkage isomerism must be recognized. As shown below, neutral phenylcyanamides (N≡C-NH-Ph) can coordinate to a metal ion through either the nitrile or the amine nitrogen:

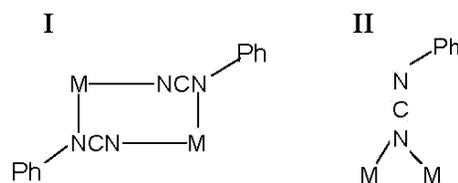


However, there are no crystal structures of neutral phenylcyanamides coordinated to metal ions. The amine nitrogen is sterically crowded by the phenyl ring and so terminal coordination to the nitrile is expected, particularly for electron-rich metal centers. Metal ions that behave as  $\pi$ -acceptors are expected to favor the anionic phenylcyanamide ligand in order to take advantage of the ligand's  $\pi$ -donor properties [12 - 14].

Side-on coordination of the cyanamide group has not been observed for phenylcyanamide ligands but has been observed in tungsten complexes of dialkylcyanamides [15]. Anionic phenylcyanamides have three non-bonding pairs of electrons that can be involved in coordination chemistry, as shown below:



There are many crystal structures of monodentate phenylcyanamide ligands showing coordination through the cyano-nitrogen but there are no examples of amide-nitrogen coordination [16 - 20]. The neutral or anionic phenylcyanamides can function as bridging ligands although this has only been observed for the anionic cyanamide:



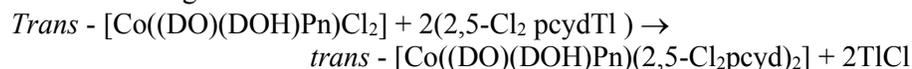
Both bridging modes I and II have been observed in copper(II) complexes [21]. At this time, only the crystal structure of Ru(II), Ru(III), Ni(II), Pd(II), Pt(II), Cu(I), Cu(II) and Ag(I) phenylcyanamide complexes have been obtained [16 - 33] and the coordination chemistry of phenylcyanamide ligands still requires much effort to complete.

## Experimental

### Preparation of *trans*-[bis(2,5-dichlorophenylcyanamido){N,N'-propanediylbis(2,3-butadien-2-imine-3-oxime)} Cobalt(III)], *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>]

[Co((DO)(DOH)pn)Cl<sub>2</sub>] [3 - 4](2×10<sup>-3</sup> mol) was dissolved in 100 mL acetonitrile in a 250mL round-bottom flask. Thallium(I)(2,5-dichlorophenylcyanamide)[13], (2,5-Cl<sub>2</sub>pcydTl) (4×10<sup>-3</sup> mol) was added, and the reaction mixture was stirred for 24 h at reflux temperature.

The Co(III) oxime complex (Fig. 1) was synthesized in good yield according to the following methathesis reaction:

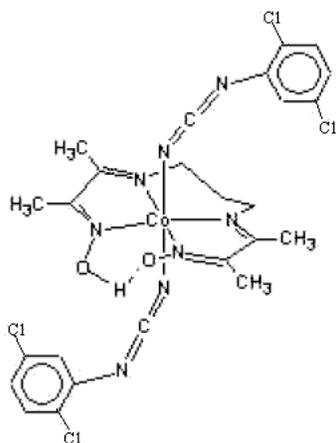


The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight. A white solid (TlCl) was filtered off. The crude brown product was precipitated from the filtrate by the addition of 500 mL of diethylether and then collected by suction filtration. Recrystallization was achieved by diffusing diethylether into an acetonitrile solution of the complex, yielding brown crystals suitable for crystallographic study.

Yield 64%. Anal. Calcd. For C<sub>25</sub>H<sub>25</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>2</sub>Co (MW = 670.275): C, 44.80; H, 3.76; N, 16.72. Found(Canadian Microanalytical Service Ltd) : C, 45.02; H, 3.81; N, 16.85.

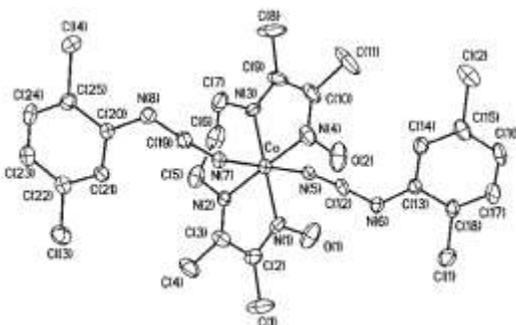
IR(KBr disk):  $\nu(\text{NCN}) = 2083 \text{ cm}^{-1}$ ; UV-vis spectra (10<sup>-3</sup>M in acetonitrile,  $\lambda$  in nm (log  $\epsilon$ ): 441(3.89), 550(3.64).

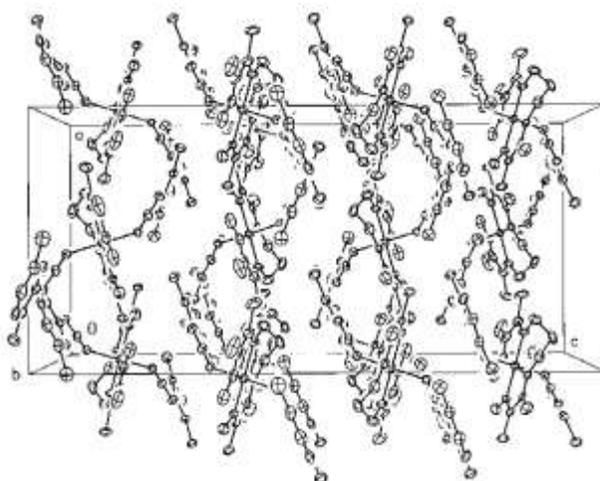
<sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>): 19.07(s,1H), 2.49(s,6H), 2.66(s,6H), 4.07(t,4H), 3.32(m,2H), 7.22(s,2H), 6.83(d,2H), 6.52(d,2H).



**Fig. 1** *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] Complex.

Crystals of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] were grown by ether diffusion into an acetonitrile solution of the complex. The data were collected on a 1 K Siemens Smart CCD using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 203(2) K using an  $\omega$ scan technique and corrected for absorptions using equivalent reflections [34]. No symmetry higher than orthorhombic was observed, and solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods and refined with full-matrix least-squares procedures. Anisotropic refinement was performed on all non-hydrogen atoms. All hydrogen atoms were calculated. Scattering factors are contained in the SHELXTL 5.1 program library [35]. The ORTEP drawings with atom numbering schemes and unit cell of the complex *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] are depicted in Figures 2 and 3. Crystal structure data, atomic coordinates, selected bond lengths and angles are given in Tables 1, 2 and 3, respectively.





**Fig. 3** Unit cell diagram of *trans*- [Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>].

**Table 1** Crystal data for *trans*- [Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>].

|   |   |
|---|---|
| Empirical Formula   | C <sub>25</sub> H <sub>25</sub> Cl <sub>4</sub> CoN <sub>8</sub> O <sub>2</sub> |
| Formula Weight  | 670.26  |
| Temperature   | 203 (2) K   |
| Wave Length   | 0.71073 Å   |
| Crystal System  | Orthorhombic  |
| Space Group   | Pbca  |
| Unit Cell Dimensions                                      | a = 13.6800 (16) Å,<br>b = 13.7434 (19) Å,<br>c = 29.892 (4) Å,                 |
| Volume  | 560.0(12) Å <sup>3</sup>  |
| Z   | 8   |
| Calculated Density  | 1.584 g/cm <sup>3</sup>   |
| Absorption Coefficient                                    | 1.032 mm <sup>-1</sup>  |
| F(000)  | 2736  |
| Crystal Size  | 0.10 × 0.10 × 0.10 mm   |
| Reflection Collected/Unique                               | 29663/2946 [R(int) = 0.3489]  |
| Absorption Correction                                     | Semi-empirical from equivalents   |
| Refinement method   | Full- matrix Least-Squares on F <sup>2</sup>                                    |
| Final R indices [I > 2<br>sigma(I)], for 2964 reflections | R <sub>1</sub> = 0.0606, wR <sub>2</sub> = 0.1292                               |
| R indices (all data) <sup>a</sup>                         | R <sub>1</sub> = 0.1401, wR <sub>2</sub> = 0.1647                               |
| Goodness-of-fit on F <sup>2</sup>                         | 1.043   |

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o| ; wR_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2)^{1/2}$$

**Table 2** Atomic coordinates ( $10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>].U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

| Atom  | x        | y       | Z       | U(eq) | Atom  | x        | y        | Z       | U(eq)  |
|-------|----------|---------|---------|-------|-------|----------|----------|---------|--------|
| Co    | 168(1)   | 5099(1) | 1281(1) | 33(1) | C(6)  | -1068(8) | 3665(8)  | 675(3)  | 72(3)  |
| Cl(1) | 3577(2)  | 7435(2) | -43(1)  | 62(1) | C(7)  | -1718(7) | 4342(8)  | 941(4)  | 69(3)  |
| Cl(2) | -5(2)    | 9794(2) | 632(1)  | 77(1) | C(8)  | -2618(7) | 6278(10) | 1083(4) | 110(5) |
| Cl(3) | -98(2)   | 463(2)  | 1955(1) | 62(1) | C(9)  | -1552(8) | 6048(8)  | 1169(3) | 60(3)  |
| Cl(4) | -3508(2) | 3156(2) | 2561(1) | 52(1) | C(10) | -869(9)  | 6798(7)  | 1351(4) | 60(3)  |
| N(1)  | 1497(5)  | 5023(6) | 1457(2) | 38(2) | C(11) | -1168(9) | 7831(7)  | 1398(4) | 104(5) |
| N(2)  | 440(5)   | 3749(5) | 1134(2) | 34(2) | C(12) | 1166(8)  | 6082(6)  | 550(3)  | 38(3)  |
| N(3)  | -1170(5) | 5192(6) | 1109(3) | 46(2) | C(13) | 1780(7)  | 7573(6)  | 337(3)  | 35(2)  |
| N(4)  | -46(6)   | 6413(5) | 1430(2) | 46(2) | C(14) | 983(7)   | 8135(6)  | 479(3)  | 46(2)  |
| N(5)  | 584(5)   | 5543(5) | 689(2)  | 35(2) | C(15) | 1010(8)  | 9128(7)  | 446(3)  | 53(3)  |
| N(6)  | 1846(5)  | 6583(5) | 370(3)  | 40(2) | C(16) | 1809(8)  | 9632(7)  | 279(3)  | 56(3)  |
| N(7)  | -225(5)  | 4688(5) | 1873(2) | 34(2) | C(17) | 2570(7)  | 9092(7)  | 135(3)  | 50(3)  |
| N(8)  | -1603(5) | 3855(5) | 2217(3) | 42(2) | C(18) | 2562(7)  | 8096(7)  | 150(3)  | 43(2)  |
| O(1)  | 1985(5)  | 5784(5) | 1615(2) | 67(2) | C(19) | -875(8)  | 4249(7)  | 2027(3) | 40(3)  |
| O(2)  | 672(6)   | 6982(5) | 1581(2) | 74(2) | C(20) | -1671(7) | 2839(6)  | 2243(3) | 35(2)  |
| C(1)  | 2995(6)  | 4068(9) | 1572(4) | 87(4) | C(21) | -924(7)  | 2203(6)  | 2125(3) | 38(2)  |
| C(2)  | 1937(7)  | 4193(8) | 1429(3) | 46(2) | C(22) | -1054(7) | 1215(6)  | 2135(3) | 43(2)  |
| C(3)  | 1273(8)  | 3445(7) | 1250(3) | 43(2) | C(23) | -1926(8) | 809(7)   | 2271(3) | 51(3)  |
| C(4)  | 1603(7)  | 2401(7) | 1235(3) | 70(3) | C(24) | -2654(7) | 1422(7)  | 2405(3) | 47(3)  |
| C(5)  | -330(7)  | 3108(7) | 955(3)  | 57(3) | C(25) | -2545(6) | 2409(7)  | 2399(3) | 39(2)  |

**Table 3** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for *trans*- [Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>].

| Bond Lengths, ( $\text{\AA}$ ) |           |               |           |
|--------------------------------|-----------|---------------|-----------|
| Co-N(4)                        | 1.883 (7) | N(5)-C(12)    | 1.165(10) |
| Co-N(1)                        | 1.896(7)  | N(6)-C(12)    | 1.274(11) |
| Co-N(3)                        | 1.905(7)  | N(6)-C(13)    | 1.368(10) |
| Co-N(7)                        | 1.935(7)  | N(7)-C(19)    | 1.170(10) |
| Co-N(2)                        | 1.942(7)  | N(8)-C(19)    | 1.267(11) |
| Co-N(5)                        | 1.956(8)  | N(8)-C(20)    | 1.400(10) |
| Bond Angles, (deg)             |           |               |           |
| N(4)-Co-N(1)                   | 97.8 (4)  | N(1)-Co-N(5)  | 89.4(3)   |
| N(4)-Co-N(3)                   | 81.4(4)   | N(3)-Co-N(5)  | 90.9(3)   |
| N(1)-Co-N(3)                   | 179.2(4)  | N(7)-Co-N(5)  | 178.5(3)  |
| N(4)-Co-N(7)                   | 91.1(3)   | N(2)-Co-N(5)  | 92.2(3)   |
| N(1)-Co-N(7)                   | 89.8(3)   | C(2)-N(1)-Co  | 118.5(7)  |
| N(3)-Co-N(7)                   | 90.0(3)   | C(3)-N(2)-Co  | 115.4(6)  |
| N(4)-Co-N(2)                   | 177.8(4)  | C(12)-N(5)-Co | 136.1(7)  |
| N(1)-Co-N(2)                   | 80.0(3)   | C(19)-N(7)-Co | 136.2(7)  |
| N(3)-Co-N(2)                   | 100.8(3)  | C(1)-N(1)-Co  | 122.5(6)  |
| N(7)-Co-N(2)                   | 88.9(3)   | C(2)-N(4)-Co  | 121.9(6)  |
| N(4)-Co-N(5)                   | 87.8(3)   |               |           |

### Results and Discussion

Trans- [Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] complex is air-stable and can be readily recrystallized. The elemental analysis of the complex is consistent with C<sub>25</sub>H<sub>25</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>2</sub>Co formula. In <sup>1</sup>H-NMR spectrum of the complex, the integration of phenyl protons of 2,5-Cl<sub>2</sub>pcyd ligands and comparison with those of ((DO)(DOH)pn) suggests that both phenylcyanamide anion ligands occupy magnetically equivalent coordination environments. In the downfield region, the intramolecular hydrogen bonding O-H---O shows a singlet at 19.07 ppm. Sufficient D<sub>2</sub>O (≈ 10 μL) was added to a DMSO-d<sub>6</sub> solution of the complex for complete D-exchange of the O-H---O signal. Under these conditions, the singlet at 19.07 ppm disappeared.

The presence of only one sharp and intense absorption band for the cyanamide stretching frequency (ν(-N=C=N)) in the complex provides evidence that both 2,5-Cl<sub>2</sub>pcyd ligands are equivalent in the solid state. When the cyanamide ligands are inequivalent, multiple ν(-N=C=N) bands are observed [10,31,34,36]. Two ligand field transitions for Co(III) complexes are expected [37]. However, the intensity of the two absorption bands in the visible region (441 and 550 nm) in comparison to Ru(III) and Co(III) phenylcyanamide complexes [16-20, 31], allow these two intense absorption bands to be assigned to the ligand to metal charge transfer(LMCT) with minor contributions to band intensity from the underlying ligand field transition. These two bands are associated with Co(III)-cyanamide chromophore. Since the t<sub>2g</sub> orbitals in Co(III) are full occupied, the LMCT bands originate from the ligand π orbital to a metal e<sub>g</sub><sup>\*</sup> (σ<sup>\*</sup>) orbitals [37].

The crystal structures of Ru(III), Ru(II), Ni(II), Pd(II), Pt(II), Cu(I), Cu(II) and Ag(I) show that the phenyl cyanamide group is an approximately planar ligand and that the preferred coordination mode of the cyanamide group is by its' terminal nitrile nitrogen [12-33]. This is likely due to the greater steric hinderance of coordination to the amide nitrogen. In addition, these crystal structures showed that when the cyanamide group is coordinated to Ru(III), the Ru(III)-cyanamide bond angle is approximately linear [10, 16-20], but, when coordinated to Ni(II), Pd(II), or Cu(II), the metal-cyanamide bond is bent [10, 21, 28, 29, 33]. In contrast to the other metal ions, Ru(III) is a π acceptor and it is only when the Ru(III)-cyanamide bond is linear that the cyanamide group can function as both a σ and π donor. Crystal structures of free dicyanamidebenzene dianion ligands [22] showed that these ligands were essentially planar and this has been ascribed to the mixing of the π systems of cyanamide and phenyl groups, and confirmed by theory.

ORTEP (Fig.2) of the complex, trans-[bis(2,5-dichlorophenylcyanamide) {N,N'-propanediylbis (2,3-butadien-2-imine-3-oxime)}Co(III)] shows the

Co(III) ion is surrounded by a distorted octahedral coordination sphere of nitrogen donor atoms. The slight differences between the nearly planar phenylcyanamide ligands and their coordination to Co(III) are probably due to crystal packing forces. The cyanamide groups are approximately linear and not significantly different as shown by the angles describing the cyanamide groups ( $\text{N}(7)\text{-C}(19)\text{-N}(18) = 173.9(10)^\circ$  and  $\text{N}(5)\text{-C}(12)\text{-N}(6) = 172.9(10)^\circ$ ). The coordination mode of the cyanamide group to Co(III) is bent as indicated by the bond angles  $\text{Co-N}(5)\text{-C}(12)$  and  $\text{Co-N}(7)\text{-C}(19)$  of  $136.1(7)^\circ$  and  $136.2(7)^\circ$ , respectively, and is therefore a reflection of Co(III)'s inability to accept  $\pi$ -electron density into a filled  $d\pi$ -orbital. There are significant differences between Co(III)-N bond lengths for the equatorial  $\{(\text{DO})(\text{DOH})\text{pn}\}$  monoanion ligand. This may be due to unequal sharing of the oxime proton as shown below. Co(III)-cyanamide bond lengths (see Table 3) are consistent with those of other first row metal ions.

### Acknowledgements

We are grateful to the USB for financial support. We also thank professor R. J. Crutchley (Carleton University) and professor G.P.A. Yap (University of Ottawa) for their fruitful discussions and comments on this manuscript.

### References:

- [1] Hadadzadeh H., Shamsipur M., Salimi A., Mousavi M.F., "Electrocatalytic activity of cobaloxime complexes adsorbed on glassy carbon electrodes toward the reduction of dioxygen", *J. Electroanal. Chem.* 517 (2001) 37-44.
- [2] Hadadzadeh H., Rezvani A.R., "Synthesis of novel mononuclear and dinuclear cobalt(III) complexes with cyanamide derivative ligands", *J. Chem. Research* No.3 (2002) 139-141.
- [3] Hadadzadeh H., Amirnasr M., "Ligand field photoaquation reactions of *trans*-  $[\text{Co}(\text{DO})(\text{DOH})\text{pn}(\text{amine})\text{Cl}]\text{PF}_6$  complexes", *Scientia Iranica* 4 (1997) 125-130.
- [4] Hadadzadeh H., Amirnasr M., "Synthesis and characterization of amine (chloro) cobaloxime derivatives, approximate values of the AOM parameter  $\sigma$  for the coordinated amines", *J. Science* 7 (1996) 164-168.
- [5] Marzilli L.G., Yohannes P.G., Bresciani-Pahor N., Randaccio L., Zangrando E., "Organocobalt  $B_{12}$  models bearing axial substituents on a *costa*-type equatorial ligand: structural, rate and spectroscopic consequences", *Inorg. Chem.* 27 (1988) 4738-4744.
- [6] Marzilli L.G., Pahor N.B., Zangrando E., Finke R.G., Myers S.A., "An assessment of the *cis*- influence in coenzyme  $B_{12}$  models", *Inorg. Chim Acta.* 107 (1985) 139-145.

- [7] Marzilli L.G., Gerli A., "Costa-type  $B_{12}$  models: synthesis, structural characterization and electrochemistry of chloro derivatives", *Inorg. Chem.* 31 (1992) 1152-1160.
- [8] Marzilli L.G., Polson M., Hansen L., Moore, S.J., Marzilli, P.A., " $B_{12}$  models with highly distorted  $N_4$  equatorial ligation and a Co-C-N ring: Structural assessment of the steric influence of benzimidazole and imidazole axial ligands", *Inorg. Chem.* 36 (1997) 3854-3860.
- [9] Marzilli L.G., Moore S.J., Kutikor A., Lachicotte R.J.L., "Methyl  $B_{12}$  models containing unsubstituted imidazole as an axial ligand investigated by structural and NMR spectroscopic methods", *Inorg. Chem.* 38 (1999) 768-776.
- [10] Crutchley R.J., "Phenylcyanamide ligands and their metal complexes", *Coord. Chem. Rev.* 219-221 (2001) 125-155.
- [11] Kabesova M., Boca R., Melnick M., Valigura D., Dunaj-jurco M., "Bonding properties of thiocyanate groups in copper(II) complexes", *Coord. Chem. Rev.* 140 (1995) 115-135.
- [12] Naklicki M.L., Crutchley R.J., "Coordination chemistry of neutral phenylcyanamide ligands bound to pentaammineruthenium(II)", *Inorg. Chem.* 28 (1989) 4226-4229.
- [13] Crutchley R.J., Naklicki M.L., "Pentaammineruthenium(III) complexes of neutral and anionic (2,3-dichlorophenyl)cyanamide: spectroscopic analysis of ligand to metal charge transfer", *Inorg. Chem.* 28 (1989) 1955-1958.
- [14] Buchanan G.W., Crutchley R.J., " $^{15}N$ -NMR study of phenylcyanamides", *Magn. Reson. Chem.* 32 (1994) 552-258.
- [15] Chisholm M.H., Foltling K., Huffman J.C., Marchant N.S., "Notable features in the molecular structure of  $W_2(OCH_2-t-Bu)_6(NCNMe_2)_3$ , *Polyhedron*", 3 (1984) 1033-1035.
- [16] Rezvani A.R., Evans C.E.B., Crutchley R.J., "Strong metal-metal coupling in a dinuclear (terpyridine)ruthenium mixed-valence complex incorporating the bridging ligand 1,4-dicyanamidobenzene dianion", *Inorg. Chem.*, 34 (1995) 4600-4604.
- [17] Rezvani A.R., Bensimon C., Cromp B., Reber C., Greedan J.E., Kondratiev V.V., Crutchley R.J., "Inner coordination sphere control of metal-metal superexchange in ruthenium dimers", *Inorg. Chem.* 36 (1997) 3322-3329.
- [18] Rezvani A.R., Crutchley R.J., "Dependence of the Ru(III)-cyanamide chromophore on inner-sphere coordination: comparison of  $cis-[Ru(bpy)_2(ncyd)_2]^+$  and  $[Ru(NH_3)_5(ncyd)]^{2+}$  complexes", *Inorg. Chem.* 33 (1994) 170-174.
- [19] Rezvani A.R., Evans C.E.B., Naklicki M.L., White C.A., Kondratiev V.V., Crutchley R.J., "An investigation of superexchange in dinuclear mixed-valence ruthenium complexes", *J. Am. Chem. Soc.* 120 (1998) 13096-13103.

- [20] Mosher P.J., Yap G.P.A., Crutchley R.J., "Influence of the inner coordination sphere on the Ru(II)-cyanamide ligand to metal charge transfer chromophore", *Inorg. Chem.* 40 (2001) 550-553.
- [21] Brader M.L., Ainscough E.W., Backer E.N., Brodie A.M., Ingham S.L., "Synthetic, spectroscopic, and X-ray crystallographic studies on phenylcyanamidocopper(II) complexes. The characterization of three different co-ordination modes for phenylcyanamide anions", *J. Chem. Soc. Dalton Trans.* (1990) 2785-2792.
- [22] Aquino M.A.S., Crutchley R.J., Lee F.L., Gabe E.J., Bensimon C., "Structure of 1,4-benzenedicyanamide dianion derivatives", *Acta Crystallogr. C* 49 (1993) 1543-1547.
- [23] Evans C.E.B., Yap G.P.A., Crutchley R.J., "Comparison of hole transfer superexchange in dinuclear mixed-valence ruthenium complexes", *Inorg. Chem.* 37 (1998) 6161-6167.
- [24] Hadadzadeh H., Rezvani A.R., "The electrochemical and spectroscopic studies of *trans*- [Co((DO)(DOH)pn)LL'] complexes", *Iran J. Chem. & Chem. Eng.* 21(2002) 21-27.
- [25] Nakliki M.L., White C.A., Kondratiev V.V., Crutchley R.J., "Mono and dinuclear ruthenium(III) and ruthenium(IV) complexes of 1,4-dicyanamido-2,5-dimethylbenzene dianion", *Inorg. Chim. Acta* 242 (1996) 63-69.
- [26] Desjardins P., Yap G.P.A., Crutchley R.J., "Tetrakis(pyridine)ruthenium *trans* complexes of phenylcyanamide ligands", *Inorg. Chem.* 38 (1999) 5901-5905.
- [27] Aquino M.A.S., Crutchley R.J., "A pentaamineruthenium mixed-valence complex with 1,4-dicyanamidobenzene dianion as bridging ligand", *Inorg. Chem.* 29(1990) 3641-3644.
- [28] Letcher R.J., Zhang W., Bensimon C., Crutchley R.J., "1,3-Bis(2'-pyridylamino)isoindolinato)nickel(II) complexes of phenylcyanamido ligands", *Inorg. Chim. Acta* 210 (1993) 183-191.
- [29] Zhang W., Bensimon C., Crutchley R.J., "(Terpyridine)palladium(II) complexes of phenylcyanamide ligands", *Inorg. Chem.* 32 (1993) 5808-5812.
- [30] Brader M.L., Ainscough E.W., Baker E.N., Brodie A.M., "Copper(II) promoted desulphurization of *N*-phenylthiourea", *Polyhedron* 8 (1989) 2219-2221.
- [31] Hadadzadeh H., Rezvani A.R., Patrick B., "Structure and spectroscopic studies of *cis*-bis(bipyridine) cobalt(III) complexes of phenylcyanamide ligands", *Inorg. Chim. Acta* 336 (2002) 125-130.
- [32] Derosa M.C., Crutchley R.J., "Semiconductor properties in an iodine-doped Pt(II) dinuclear complex", *Inorg. Chem.* 40 (2001) 1406-1407.

- [33] Ainscough E.W., Backer E.N., Brader M.L., Brodie A.M., Ingham S.L., Waters J.M., Hanna J.V., Healy P.C., *"Synthetic, spectroscopic and X-ray crystallographic studies on phenylcyanamidocopper(I) complexes"*, J. Chem. Soc. Dalton Trans. (1991) 1243-1250.
- [34] Blessing R., *"An empirical correction for absorption anisotropy"*, Acta Crystallogr. A51 (1995) 33-38.
- [35] Sheldrick G.M., *"SHELXTL 5.1"*, Bruker AXS Inc., Madison, WI (1997).
- [36] Mosher P.J., Yap G. P. A., Crutchley R.J., *"A donor-acceptor-donor bridging ligand in a class III mixed-valence complex"*, Inorg. Chem. 40 (2001) 1189-1195.
- [37] Lever A.B.P., *"Inorganic Electronic Spectroscopy"*, 2<sup>nd</sup> ed. (1984) Elsevier, Amsterdam.