

ساختار بلوری کمپلکس (۲، ۲'-بی پیریدین) (۲، ۵-دی کلروفنیل سیانامیدو) (۲، ۲':۶، ۶'-تریپیریدین) رودیم (III) هگزافلوئوروفسفات [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂·0.5CH₃CN

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(دریافت مقاله ۸۳/۱۱/۳، دریافت نسخه نهایی ۸۴/۲/۷)

چکیده: نخستین ساختار بلوری کمپلکس فنیل سیانامید رودیم (III) با فرمول [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂·0.5CH₃CN گزارش شده است. بلورهای [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂·0.5CH₃CN به وسیله نفوذ اتر به داخل محلول استونیتریلی کمپلکس رشد داده شد. داده‌های ساختار بلوری به صورت زیر می‌باشد: سیستم تبلور از نوع اورتورومبیک و گروه فضائی Fdd2 است.

$a = 84.228(3)$, $b = 8.7162(3)$, $c = 21.4921(7)$ Å, $V = 15778.4(9)$ Å³, and $Z = 16$. ساختار بر اساس ۴۹۷۱ انعکاس مستقل با $R_w = 0.1752$ و $R = 0.0644$, $I > 2\sigma(I)$ به دست آمد. ORTEP مربوط به کمپلکس [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂·0.5CH₃CN نشان می‌دهد که سه حلقه پیریدیلی لیگاند تریپیریدین و دو حلقه لیگاند بی‌پیریدین به وسیله اتمهای نیتروژن خود به رودیم (III) کوئوردینه شده‌اند. گروه آنیونی سیانامید به صورت انتهائی و به وسیله نیتروژن نیتریلی خود به یون رودیم (III) کوئوردینه شده است. پیوند Rh^{III}-NCN خمیده و زاویه آن ۱۲۵/۴° است.

واژه‌های کلیدی: لیگاند فنیل سیانامید، کمپلکس رودیم (III)، حلقه پیریدیلی، بی پیریدین، تریپیریدین.

Crystal Structure of (2,2'-bipyridine) (2,5-dichlorophenylcyanamido) (2,2':6',2''-terpyridine)rhodium(III) Hexafluorophosphate, [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂.0.5CH₃CN

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(Received: 23/1/2005, received in revised form: 27/4/2005)

Abstract: The first crystal structure of a phenylcyanamide Rh(III) complex, [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂ (terpy = 2,2':6',2''- terpyridine, bpy= 2,2'-bipyridine, and 2,5-Cl₂pcyd = 2,5-dichlorophenylcyanamide) has been reported in this paper. Crystals of [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂.0.5CH₃CN were grown by ether diffusion into an acetonitrile solution of the complex. Crystal structure data: orthorhombic system, space group Fdd2, with a = 84.228(3), b = 8.7162(3), c = 21.4921(7) Å, V=15778.4(9) Å³, and Z=16. The structure was refined by using 4971 independent reflections with I>2σ(I) to a R factor of 0.0644 and R_w = 0.1752. ORTEP drawing of [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂.0.5CH₃CN shows that the terpy and bpy ligands are coordinated to the Rh^{III} through their nitrogen atoms in a mutually perpendicular fashion. The anionic cyanamide group is coordinated end-on by the nitrile nitrogen to the Rh^{III}. The Rh^{III}-NCN bond is bent, having an angle of 125.4°. This bent bond is largely determined by the σ-bonding interaction of a cyanamide non-bonding electron pair in a sp² hybrid orbital.

Keywords: Phenylcyanamide Ligands, Rhodium (III) Complex, Pyridyl Ring, Bipyridine, Terpyridine.

Introduction

Interest in Cyanamide ligands began with the discovery of copper salts of radical anion N,N'-dicyanoquiondiimine derivatives (DCNQI). The Cu(DCNQI)₂ molecular models show evidence of being three dimensional conductors in that they have conductivity not only in the direction of the π -stacks but also in the direction of the Cu-cyanamide links between the π -stacks[1]. The phenylcyanamides are ambidentate ligands whether neutral or in anionic form and so the possibility of linkage isomerism must be recognized. The coordination chemistry of phenylcyanamide ligands still requires much effort to complete. Up to now, only the crystal structures of Ru^{II}, Ru^{III}, Ni^{II}, Pd^{II}, Cu^{II}, Cu^I, Ag^I and Co^{III} phenylcyanamide complexes have been obtained [2-24]. In this study, the Rh(III) complex, [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂·0.5CH₃CN has been prepared and characterized by elemental analysis, IR, ¹H NMR and UV-Vis spectroscopies. A crystal structure determination of the complex has been performed and compared with the structures of other transition metal complexes of phenylcyanamide ligands.

Experimental

Materials and general methods

All reagents and solvents used in this study were reagent grade or better. [Rh(terpy)(bpy)Cl](PF₆)₂ [25] and the thallium salts of phenylcyanamide ligands [4] were synthesized according to literature procedures. Caution: Thallium is toxic.

Elemental analyses were performed by Heraeus CHN-O-Rapid elemental analyzer. IR spectra were measured on a Shimadzu 460 spectrophotometer with KBr pellets and electronic spectra on a JASCO 7850 spectrophotometer. ¹H NMR spectra were recorded on a Bruker DRX-500 MHz AVANCE spectrometer at ambient temperature in DMSO-d₆.

Preparation of (2 , 2'- bipyridine) (2 , 5 – dichlorophenylcyanamido) (2 , 2':6', 2''– terpyridine) rhodium (III) Hexafluorophosphate, [Rh (terpy) (bpy) (2,5-Cl₂pcyd)] (PF₆)₂·0.5CH₃CN

A mixture of [Rh (terpy) (bpy)Cl] (PF₆)₂ (1mmol) and 2,5-Cl₂pcydTl (1 mmol) dissolved in 25 mL of N,N'- dimethylformamide (DMF) and was stirred at reflux temperature overnight. The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight. The white solid (TlCl) was filtered off. The crude product precipitated as a yellow-orange solid with the addition of 200mL of diethylether to the filtrate, then was collected by suction filtration. Recrystallization was achieved by the slow diffusion of diethylether into a saturated solution of the crude complex in CH₃CN.

[Rh (terpy) (bpy)Cl] (PF₆)₂ + 2,5 - Cl₂pcydTl → [Rh (terpy) (bpy) (2,5-Cl₂pcyd)](PF₆)₂ + TlCl↓

Yield 64%. Anal. Calcd. For C₃₂H₂₂Cl₂F₁₂N₇P₂Rh (Vacuum dried) (MW = 968.3134): C, 39.70; H, 2.29; N, 10.13. Found: C, 40.05; H, 2.34; N, 10.30.

IR(KBr disk): $\nu(\text{NCN}) = 2097 \text{ cm}^{-1}$; UV-vis spectra (10^{-3}M in acetonitrile, λ in nm (log ϵ)): 504(3.73), 320(3.38), 281(4.27), 265(4.96), 237(3.85).

$^1\text{H-NMR}$ (500 MHz, DMSO-d_6): 6.15(s), 6.85(d), 7.16(d), 7.53(t), 7.82(m), 8.11(d), 8.25(t), 8.41(m), 8.56(t), 8.69(t), 8.77(d), 8.89(d), 9.09(d), 9.27(d), 9.48(t).

Yellow crystals of $[\text{Rh}(\text{terpy})(\text{bpy})(2,5\text{-Cl}_2\text{pcyd})](\text{PF}_6)_2 \cdot 0.5\text{CH}_3\text{CN}$ were grown by ether diffusion into an acetonitrile solution of the complex. Single-crystal X-ray diffraction measurements were carried out with a BRUKER AXS SMART 2K/platform diffractometer equipped with a graphite monochromator for data collection at 220(2)K. The determination of unit cell dimensions and data collection was performed with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178\text{\AA}$). Data reduction processing was carried out by the use of the program SAINT [26], which applied Lorentz and Polarization corrections to the three-dimensionally integrated diffraction spots. The program SADABS [27] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

The space group was confirmed by XPREP routine in SHELXTL program [28]. The structure was solved by direct method using SHELXS97 [29] and difmap synthesis using SHELXL97[30]. All non-H atoms anisotropic, where all refined hydrogen atoms isotropic. H atoms constrained to the parent site using a riding model; SHELXL97 defaults, C-H 0.94 to 0.97 $\text{\AA}$. The isotropic factors, U_{iso} , were adjusted to 50% higher value of the parent site(methyl) and 20% higher (others). A final verification of possible voids was performed using the VOID routine of the PLATON program [31]. Crystal structure data, atomic coordinates, selected bond lengths and angles are given in Tables 1 and 3, respectively.

Table 1 Crystallographic data and structure refinement summary for $[\text{Rh}(\text{terpy})(\text{bpy})(2,5\text{-Cl}_2\text{pcyd})](\text{PF}_6)_2 \cdot 0.5\text{CH}_3\text{CN}$

Formula	$\text{C}_{33}\text{H}_{23}\text{Cl}_2\text{F}_{12}\text{N}_7\text{P}_2\text{Rh}$
Molecular weight	988.84
Crystal system	Orthorhombic
Space group	$Fdd2$
Unit cell dimensions($\text{\AA}$)	$a = 84.2280(30)$
	$b = 8.7162(3)$
	$c = 21.4921(7)$
Volume($\text{\AA}^3$)	15778.4(9)
Z	16
D_{calc} (g/cm^3)	1.665
μ (mm^{-1})	6.368
Crystal size(mm)	$0.45 \times 0.14 \times 0.03$
Range of h, k, l	$-90/89, -9/9, -22/22$
Reflections collected/unique	48988/4971
Parameters	713
R and R_w	0.0644, 0.1752
Residual electron densities($\text{e/\AA}^3$)	1.489 to -0.957
Goodness of fit	1.051

Table 2 Atomic coordinates($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Rh}(\text{terpy})(\text{bpy})(2,5\text{-Cl}_2\text{pcyd})](\text{PF}_6)_2 \cdot 0.5\text{CH}_3\text{CN}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Rh	9227(4)	4929(10)	8333(7)	33(3)
N11	9224(9)	2769(9)	8728(4)	35(2)
C12	9099(1)	1897(12)	8833(5)	45(3)
C13	9111(8)	494(11)	9141(5)	45(3)
C14	9258(9)	15(12)	9300(7)	60(4)
C15	9394(1)	888(10)	9181(5)	53(3)
C16	9371(9)	2326(12)	8898(6)	53(3)
C17	9501(5)	3388(11)	8778(6)	55(3)
N18	9453(3)	4673(8)	8484(4)	43(3)
C19	9549(8)	5820(12)	8362(7)	62(3)
C110	9711(6)	5708(16)	8479(10)	104(6)
C111	9766(1)	4389(19)	8782(11)	126(7)
C112	9659(2)	3203(16)	8926(9)	70(3)
C113	9465(7)	7182(12)	9119(1)	114(1)
N114	9306(4)	7019(9)	8081(6)	50(3)
C115	9222(1)	8172(12)	8013(4)	38(2)
C116	9291(2)	9506(14)	7759(1)	57(1)
C117	9451(2)	9694(12)	550(3)	82(1)
C118	9541(9)	8498(13)	7649(7)	79(2)
N21	8991(10)	5167(8)	7896(7)	80(1)
C22	8882(1)	5808(11)	7936(3)	27(2)
C23	8728(11)	5990(11)	8490(5)	50(1)
C24	8685(1)	5526(12)	8308(6)	57(1)
C25	8798(4)	4865(12)	7721(5)	52(1)
C26	8953(3)	4691(10)	7551(5)	34(2)
C27	7078(11)	3996(11)	7187(4)	35(3)
N28	9224(9)	4106(9)	7459(4)	40(2)
C29	9347(4)	3558(12)	7143(5)	48(3)
C210	9339 (4)	2855(15)	6561(5)	65(4)
C211	9189(7)	2754(16)	6292(5)	65(4)
C212	9058(1)	3340(13)	6603(4)	47(3)
N31	9212(4)	5832(10)	9222(5)	39(2)
C32	9219(11)	5118(11)	9687(6)	35(3)
N33	9214(1)	4375(11)	10192(4)	39(2)
C34	9347(2)	3950(4)	10506(17)	48(8)
C35	9341(3)	2740(3)	10954(15)	63(8)
C36	9475(3)	2330(4)	11256(16)	65(8)
C37	9620(3)	2960(3)	11181(12)	63(8)
C38	9629(2)	4100(2)	10735(11)	52(6)
C39	9493(3)	4640(3)	10426(12)	53(7)
C135	9162(3)	1840(3)	11073(15)	93(7)
C138	9814(1)	4883(11)	10581(4)	96(2)
C44	9351(2)	3830(4)	10460(17)	46(7)
C45	9336(3)	2790(3)	10971(15)	64(8)
C46	9467(3)	2140(4)	11224(16)	64(8)
C47	9619(3)	2440(3)	11042(12)	73(1)
C48	9635(2)	3400(3)	10532(11)	54(7)
C49	9504(2)	410(3)	10251(12)	65(1)
C145	9149(3)	2340(3)	11237(15)	96(2)
C148	9824(7)	3702(12)	10229(4)	47(1)
P1	8772(7)	297(3)	7680(7)	85(2)
F11	8727(7)	1776(9)	8101(4)	75(2)
F12	8948(6)	1022(8)	7602(4)	90(2)
F13	8728(2)	1165(11)	7052(4)	104(3)
F14	8606(5)	-422(11)	7746(5)	92(3)
F15	8829(6)	-550(8)	8285(4)	79(2)
F16	8825(4)	-1178(8)	7286(4)	59(3)
P2	9995(3)	140(2)	8802(9)	54(8)
F21	9872(3)	650(3)	8269(11)	31(6)

Table 3 Selected bond lengths (Å) and angles (°) for [Rh(terpy)(bpy)(2,5-Cl₂pcyd)](PF₆)₂·0.5CH₃CN

<i>Bond lengths</i>			
Rh-N(18)	1.942 (8)	Rh-N(114)	2.057 (8)
Rh-N(28)	2.013(9)	Rh-N(11)	2.065(8)
Rh-N(21)	2.046(7)	Rh-N(31)	2.068(9)
N(11)-C(12)	1.324(12)	P(1)-F(14)	1.540(9)
N(11)-C(16)	1.348(12)	P(1)-F(15)	1.569(8)
N(21)-C(26)	1.336(11)	P(1)-F(13)	1.593(9)
N(21)-C(22)	1.340(11)	P(1)-F(16)	1.603(8)
N(28)-C(29)	1.396(13)	P(1)-F(12)	1.619(7)
N(31)-C(32)	1.264(15)	P(1)-F(11)	1.619(7)
<i>Bond angles</i>			
N(18)-Rh-N(28)	97.4 (4)	N(28)-Rh-N(31)	175.4(3)
N(18)-Rh-N(21)	176.7(3)	N(21)-Rh-N(31)	96.2(3)
N(28)-Rh-N(21)	79.3(3)	N(114)-Rh-N(31)	89.6(4)
N(18)-Rh-N(114)	80.8(3)	N(11)-Rh-N(31)	88.1(4)
N(28)-Rh-N(114)	90.4(3)	C(12)-N(11)-C(16)	121.6(9)
N(21)-Rh-N(114)	98.6(3)	C(12)-N(11)-Rh	127.0(7)
N(18)-Rh-N(11)	80.6(3)	C(16)-N(11)-Rh	111.3(6)
N(28)-Rh-N(11)	93.3(3)	C(19)-N(18)-Rh	119.0(6)
N(21)-Rh-N(11)	100.0(3)	C(17)-N(18)-Rh	118.0(6)
N(114)-Rh-N(11)	161.4(3)	C(32)-N(33)-C(34)	122.6(1)
N(18)-Rh-N(31)	87.1(4)	N(31)-C(32)-N(33)	175.3(1)

Results and discussion

Figure 1 shows the coordination geometry of the ligands about the Rh^{III}. The crystal structure shows that the terpy and bpy ligands are coordinated to the Rh^{III} through their nitrogen atoms in a mutually perpendicular fashion.

As shown by ORTEP of the complex (Fig.1), the geometry about the Rh^{III} is distorted-octahedral where three nitrogen atoms of the terpy ligand [N(11), N(18) and N(114)] and one nitrogen atom [N(21)] of the bpy ligand form the equatorial base. The remaining nitrogen atom [N(28)] of the bpy ligand and the nitrile nitrogen [N(31)] of the 2,5-Cl₂pcyd ligand are in the axial position with the Rh-N(31) distance of 2.068(9) Å and the bond angle formed by those atoms [N(28)-Rh-N(31)] is 175.4(3)°. The average bond length between the Rh^{III} and each nitrogen atom [N(11), N(18) or N(114)] of the terpy ligand is 2.022(13) Å with the middle nitrogen atom and Rh^{III} distance [Rh-N(18)] being the shortest (1.942(8) Å). The average bond angle of 80.7(3)° formed by two nitrogen atoms of the terpy ligand and Rh^{III} [N(11)-Rh-N(18), N(114)-Rh-N(18)] is slightly larger than that formed by two nitrogen atoms of the bpy ligand and Rh^{III} [N(21)-Rh-N(28)] in the cis position [79.3(3)°]. These results are similar to the one obtained by Seok et al. for [Rh(terpy)(bpy)Cl](PF₆)₂ [25].

The crystal structures of Ru^{II}, Ru^{III}, Ni^{II}, Pd^{II}, Cu^{II}, Cu^I, Ag^I and Co^{III} phenylcyanamide complexes show that the phenylcyanamide group is an

approximately planar ligand and that the preferred coordination mode of the cyanamide group is by its' terminal nitrile nitrogen [1-24]. This is likely due to the greater steric hindrance of coordination to the amide nitrogen. In addition, these crystal structures showed that when the cyanamide group is coordinated to Ru^{III} , the $\text{Ru}^{\text{III}} - \text{cyanamide}$ bond angle ($\text{Ru}-\text{NCN}$) is approximately linear, having an angle of 171.4° but, when coordinated to Ni^{II} , Pd^{II} , Cu^{II} or Co^{III} , the metal-cyanamide bond is bent [1,9,12,19,20,22]. For example, $\text{Pd}-\text{NCN}$ bond angle is 137.9° [20]. In contrast to the other metal ions, Ru^{III} is a π acceptor and it is only when the $\text{Ru}^{\text{III}} - \text{NCN}$ bond is linear that the cyanamide group can function as both a σ and π donor [1]. Crystal structure data for $[\text{Rh}(\text{terpy})(\text{bpy})(2,5-\text{Cl}_2\text{pcyd})](\text{PF}_6)_2$ show that the coordination mode of the cyanamide group to Rh^{III} ion is bent as indicated by the bond angle $\text{Rh}-\text{N}(31)-\text{C}(32)$ of $125.4(7)^\circ$, and is therefore a reflection of Rh^{III} 's inability to accept π -electron density into a filled $d\pi$ -orbital. The bent $\text{Rh}^{\text{III}}-\text{NCN}$ bond is largely determined by the σ -bonding interaction of a cyanamide non-bonding electron pair in a sp^2 hybrid orbital.

The Rh^{III} -cyanamide bond length of $2.068(9) \text{ \AA}$ is larger than the average Ru^{III} -cyanamide bond length of $1.97(2) \text{ \AA}$ that was derived from six Ru^{III} -cyanamide structures [1,8,14,17]. The shorter Ru^{III} bond distance indicates significant π bonding in Ru^{III} -cyanamide bonds. π donation of the cyanamide group to Rh^{III} is not possible because of its d^6 electron configuration.

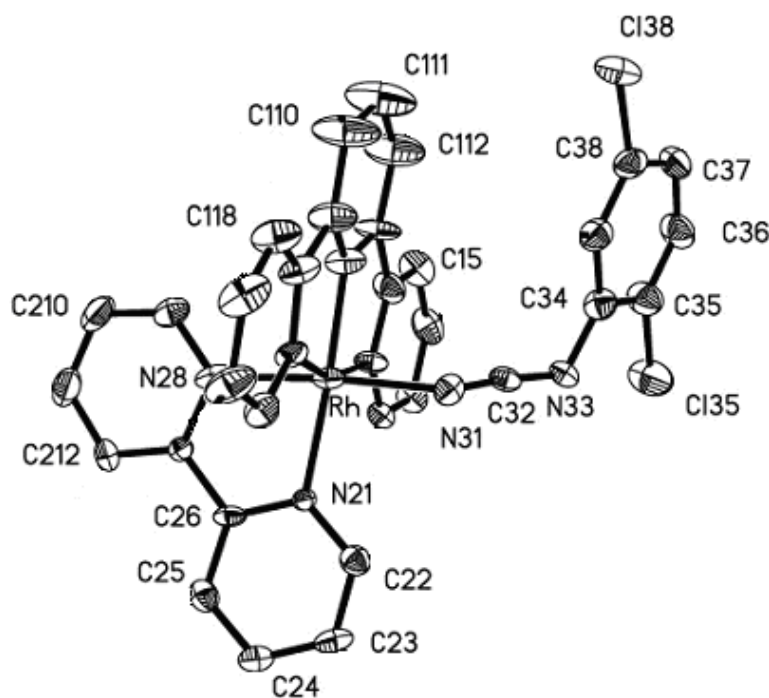


Fig. 1 ORTEP structure of the $[\text{Rh}(\text{terpy})(\text{bpy})(2,5-\text{Cl}_2\text{pcyd})]^{2+}$ cation.

Acknowledgements

The authors are grateful to the USB for financial support.

References

- [1] Crutchley R. J., *"Phenylcyanamide ligands and their metal complexes"*, Coord. Chem. Rev. 219-221 (2001) 125-155.
- [2] 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.
- [3] Naklicki M. L., Crutchley R. J., *"Coordination chemistry of neutral phenylcyanamide ligands bound to pentaammineruthenium(II)"*, Inorg. Chem. 28 (1989) 4226-4229.
- [4] 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.
- [5] Buchanan G. W., Crutchley R. J., *"¹⁵N-NMR study of phenylcyanamides"*, Magn. Reson. Chem. 32 (1994) 552-258.
- [6] Chisholm M. H., Folting K., Huffman J. C., Marchant N. S., *"Notable features in the molecular structure of W₂(OCH₂-t-Bu)₆(NCNMe₂)₃, Polyhedron"*, 3 (1984) 1033-1035.
- [7] 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.
- [8] Rezvani A. R., Bensimon C., Crompt B., Reber C., Greedan J. E., Kondratiev V. V., Crutchley R. J., *"Inner coordination sphere control of metal-metal superexchange in ruthenium dimmers"*, Inorg. Chem. 36 (1997) 3322-3329.
- [9] Rezvani A. R., Crutchley R. J., *"Dependence of the Ru(III)-cyanamide chromophore on inner-sphere coordination: comparison of cis-[Ru(bpy)₂(pcyd)₂]⁺ and [Ru(NH₃)₅(pcyd)]²⁺ complexes"*, Inorg. Chem. 33 (1994) 170-174.
- [10] 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.

- [11] 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.
- [12] 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.
- [13] Aquino M. A. S., Crutchley R.J., Lee F.L., Gabe E.J., Bensimon C., "Structure of 1,4- benzenedicyanamide dianion derivatives, *Acta Crystallogr*", C49 (1993) 1543-1547.
- [14] 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.
- [15] 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.
- [16] 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 –5-dimethylbenzene dianion", *Inorg. Chim. Acta*, 242 (1996) 63-69.
- [17] Desjardins P., Yap G.P.A., Crutchley R.J., "tetrakis(pyridine)ruthenium trans complexes of phenylcyanamide ligands", *Inorg. Chem.* 38 (1999) 5901-5905.
- [18] 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.
- [19] 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.
- [20] Zhang W., Bensimon C., Crutchley R. J., "(Terpyridine)palladium(II) complexes of phenylcyanamide ligands", *Inorg. Chem.* 32 (1993) 5808-5812.
- [21] Brader M. L., Ainscough E. W., Baker E. N., Brodie A. M., "Copper(II) promoted desulphurization of N-phenylthiourea", *Polyhedron* 8 (1989) 2219-2221.
- [22] 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.

- [23] Derosa M. C., Crutchley R. J., *"Semiconductor properties in an iodine-doped Pt(II) dinuclear complex"*, Inorg. Chem. 40 (2001) 1406-1407.
- [24] 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.
- [25] Kim M. Y., Seok W. K., Dong Y., Yun H., *"Crystal structure and electrochemical behavior of Rh polypyridyl complexes"*, Inorg. Chim. Acta 319 (2001) 194-198.
- [26] SAINT Release 6.06, *"Integration Software for Single Crystal Data"*, Bruker AXS Inc., Madison (1999).
- [27] Sheldrick G. M., SADABS, *"Bruker Area Detector Absorption Corrections"*, Bruker AXS Inc., Madison (1996).
- [28] SHELXTL Release 5.10, *"The Complete Software Package for Single Crystal Structure Determination"*, Bruker AXS Inc., Madison, (1997).
- [29] Sheldrick G. M., *"SHELXS97, Program for Crystal Structure Solution"*, University of Göttingen, Germany (1997).
- [30] Sheldrick G. M., *"SHELXL97, Program for Crystal Structure refinement"*, University of Göttingen, Germany (1997).
- [31] Spek A. L., *"PLATON, Molecular Geometry Program"*, University of Utrecht, Utrecht, Holland (2000).