Inorganica Chimica Acta, *214* (1993) 41–45

Ruthenium carbonyl complexes of N-heterocyclic molecules Part 3*. Synthesis of ruthenium complexes of the ambidentate ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (APT). X-ray crystal structures of two coordination isomers of $Ru(CO)_2Cl_2(APT)$

Arnold L. Rheingold**
Department of Chemistry, University of Delaware, Newark, DE 19716 (USA)

Patsy Saisuwan and Nicholas C. Thomas**
Department of Physical Sciences, Auburn University at Montgomery, Montgomery, AL 36117 (USA)

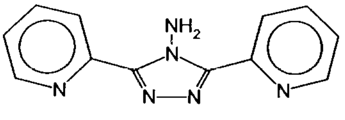
(Received February 25, 1993; revised July 13, 1993)

Abstract

4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (APT), a poly- and ambidentate ligand, forms two bidentate coordination isomers of $Ru(CO)_2Cl_2$, which in one case is coordinated to a pyridyl ring and an adjacent triazole ring (**A**), and in the other case to a pyridyl ring and the amino nitrogen atom (**B**). Both isomers of $Ru(CO)_2Cl_2(APT)$ have been crystallographically characterized: **A**, orange, orthorhombic, *Pbca*, $a = 15.332(4)$, $b = 17.715(4)$, $c = 13.083(4)$ Å, $R(F) = 3.26\%$; **B**(MeOH), yellow, triclinic, $P\bar{1}$, $a = 8.712(2)$, $b = 9.492(2)$, $c = 12.142(2)$ Å, $\alpha = 86.03(2)$, $\beta = 82.63(2)$, $\gamma = 74.21(2)°$, $R(F) = 3.49\%$. The complexes are formed directly from the reaction of $[Ru(CO)_2Cl_2]_n$ with APT in boiling MeOH. In a similar reaction with $Re(CO)_5Cl$, $Re(CO)_3Cl(APT)$ is formed. The Br analogue of the Ru complex forms predominantly the yellow isomer (**B**), while the I analogue crystallizes only as the orange isomer (**A**). Based on NMR data, the Re complex most likely coordinates via the **A** mode.

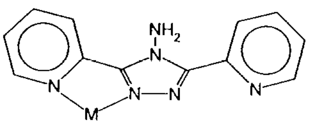
Introduction

Although first prepared [2] in 1960, the coordination chemistry of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (APT) has only been recently and briefly studied [3–5].

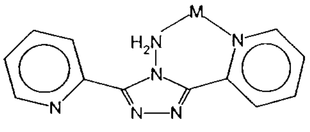


APT

Spectroscopic and X-ray crystallographic studies of nickel [3], rhodium [4], manganese [5] and copper [6] complexes show that the APT ligand can act as either a monodentate ligand, or, more commonly, as a bidentate, chelating ligand. In the bidentate mode, ambidentate behavior is found in two combinations of nitrogen donor atoms; in one, a metal atom is coordinated to a pyridyl ring and an adjacent triazole ring (**A**), and in the other to a pyridyl ring and the amino nitrogen atom (**B**).



A



B

To date, all crystallographic studies have been of examples of the **A** mode. In the present study, we describe the synthesis and spectroscopic studies of new ruthenium and rhenium carbonyl complexes containing the APT ligand, and we have obtained X-ray crystallographic structures of both modes of APT bidentate chelation of $RuCl_2(CO)_2$. These coordination isomers comprise a rare example of structurally characterized ambidentate ligand behavior with the same metal moiety.

Experimental

Microanalyses were performed by Galbraith Laboratories, Tennessee. IR spectra (4000–600 cm^{-1}) were recorded as Nujol mulls between NaCl plates with a Perkin-Elmer 167 spectrophotometer. NMR spectra were recorded in DMSO-d_6 with a Bruker AM 400 spectrometer. Aromatic NMR assignments are based

---

*For Part 2 see ref. 1.

**Authors to whom correspondence should be addressed.

0020-1693/93/$6.00

on a comparison with the spectra of the free ligand and those made for related rhodium complexes [4]. Protons in the coordinated pyridyl rings are designated as $H_{3',4',5',6'}$.

All reactions were carried out in air. Solvents were HPLC grade (Aldrich). The ruthenium compound $[Ru(CO)_2Cl_2]_n$ was prepared by the literature method [7] and $Re(CO)_5Cl$ and APT were obtained from Aldrich and used as received.

*Preparation of $Ru(CO)_2Cl_2(APT)$ complexes (**IA**, Cl and **IB**, Cl·MeOH)*

A solution of $[Ru(CO)_2Cl_2]_n$ (0.20 g) in methanol (15 ml) was boiled for 5 min and filtered into a solution of APT (0.30 g) in methanol (15 ml). The mixture was gently boiled for 5 min, filtered and allowed to cool slowly to room temperature. On standing for several hours a product consisting of a mixture of yellow and orange crystals precipitated. These were collected by filtration and separated by hand. The products were separately recrystallized from methanol/dichloromethane. Yield of the yellow isomer (**IB**, Cl) 35%. *Anal.* Calc. for $C_{14}H_{10}Cl_2N_6O_2Ru \cdot CH_3OH$: C, 36.15; H, 2.83; N, 16.87. Found: C, 36.06; H, 2.83; N, 16.93%. IR: 2066s, 2016s cm^{-1}. ^{1}H NMR: δ 10.77 (s, NH_2), 9.14 (d, $H_{6'}$), 8.85 (d, H_6), 8.45 (d, $H_{3'}$), 8.32 (m, $H_{3',4'}$), 8.16 (dd, $H_{4'}$), 7.89 (dd, $H_{5'}$), 7.69 (dd, H_5), 3.16 (s, CH_3). Yield of orange isomer (**IA**, Cl) 30%. *Anal* Calc. for $C_{14}H_{10}Cl_2N_6O_2Ru \cdot CH_3OH$: C, 36.15; H, 2.83; N, 16.87. Found: C, 36.25; H, 2.83; N, 17 04%. IR: 2073s, 2005s cm^{-1}. ^{1}H NMR: δ 9.30 (d, $H_{6'}$), 9.01 (d, $H_{3'}$), 8.85 (d, H_6), 8.46 (dd, $H_{4'}$), 8.34 (d, H_3), 8.14 (dd, H_4), 7.92 (dd, $H_{5'}$), 7.70 (dd, H_5), 7.51 (s, NH_2); methanol peak was obscured by the solvent

*Preparation of $Ru(CO)_2Br_2(APT) \cdot CH_3OH$ (**IB**, Br)*

A mixture of $[Ru(CO)_2Cl_2]_n$ (0.20 g) and LiBr (0.80 g) in methanol (20 ml) was boiled gently for 30 min. The resultant solution was filtered into a solution of APT (0.40 g) in methanol (15 ml) and the mixture was treated as above for the chloro complex to give yellow crystals. Yield 45%. *Anal.* Calc. for $C_{14}H_{10}Br_2N_6O_2$-$Ru \cdot CH_3OH$: C, 30 68; H, 2.40; N, 14.32. Found. C, 31 17; H, 2.32; N, 14.58%. IR: 2073s, 2005s cm^{-1}. ^{1}H NMR: δ 10 62 (s, NH_2), 9.20 (d, $H_{6'}$), 8.85 (d, H_6), 8.50 (d, $H_{3'}$), 8.36 (dd, $H_{4'}$), 8.25 (d, H_3), 8.16 (dd, $H_{4'}$), 7.88 (dd, $H_{5'}$), 7.68 (dd, H_5), 3.16 (s, CH_3).

*Preparation of $Ru(CO)_2I_2(APT)$ (**IA**, I)*

This was prepared as above using LiI in place of LiBr. Yield 55%. *Anal.* Calc. for $C_{14}H_{10}I_2N_6O_2Ru$: C, 25.90; H, 1.55; N, 12.95. Found: C, 26.09; H, 1.53; N, 12.89%. IR: 2056s, 2000s cm^{-1}. ^{1}H NMR. δ 9.26 (d, $H_{6'}$), 9.01 (d, $H_{3'}$), 8.84 (d, H_6), 8.39 (dd, $H_{4'}$), 8.32 (d, H_3), 8.14 (dd, H_4), 7.85 (dd, $H_{5'}$), 7.70 (dd, H_5), 7.52 (s, NH_2).

*Preparation of $Re(CO)_3Cl(APT)$ (**II**)*

A solution of $Re(CO)_5Cl$ (0.20 g) in toluene (15 ml) was added to a solution of APT (0.25 g) in toluene (15 ml). The mixture was gently boiled for several minutes during which time a yellow solid precipitated. After cooling the product was collected by filtration and recrystallized from acetone/ethanol. Yield 60%. *Anal.* Calc. for $C_{15}H_{10}ClN_6O_3Re$: C, 33.12; H, 1.85; N, 15.45. Found: C, 32.88; H, 1.74; N, 15.23%. IR: 2025s, 1915s, 1880s cm^{-1}. ^{1}H NMR: δ 9.09 (d, $H_{6'}$), 8.92 (d, $H_{3'}$), 8.84 (d, H_6), 8.41 (dd, $H_{4'}$), 8.30 (d, H_3), 8.14 (dd, H_4), 7.82 (dd, $H_{5'}$), 7.70 (dd, H_5), 7.43 (s, NH_2).

*X-ray crystal structure determination of **IA**(Cl) and **IB**(Cl)·CH_3OH*

Crystal data for both compounds are collected in Table 1. Both the yellow crystals of compound **IB**(Cl) and the orange crystals of compound **IA**(Cl) were mounted on glass fibers. Photographic analysis revealed $\bar{1}$ Laue symmetry for **IB**(Cl) and *mmm* Laue symmetry for **IA**(Cl). The centrosymmetric space group choice for **IB**(Cl) was confirmed by the well behaved solution and refinement of the structure. A semi-empirical correction for absorption was applied to compound **IA**(Cl) ($T_{max} T_{min}$ = 0.3363/0.3148). No correction for absorption was applied to compound **IB**(Cl).

Both structures were solved by direct methods. In both compounds, all non-hydrogen atoms were refined

TABLE 1 Crystallographic data for $Ru(CO)_2Cl_2(APT)$

	Isomer **IA**	Isomer **IB**
Formula	$C_{14}H_{10}Cl_2N_6O_2Ru$	$C_{14}H_{10}Cl_2N_6O_2Ru$ CH_3OH
Formula weight	466 3	498 3
Space group	*Pbca*	$P\bar{1}$
a (Å)	15 332(4)	8.712(2)
b (Å)	17 715(4)	9.492(2)
c (Å)	13 083(4)	12.142(2)
α (°)		86 03(2)
β (°)		82.63(2)
γ (°)		74 21(2)
V (Å^3)	3553 4(18)	957 5(4)
Z	8	2
D_{calc} (g/cm^3)	1 743	1 728
μ(Mo Kα) (cm^{-1})	12 04	11 11
T (°C)	26	25
Radiation	Mo Kα (λ = 0 71073 Å)	
$R(F)^a$ (%)	3 26	3 49
$R_w(F)^b$ (%)	4 56	5 15

$^a R(F_o) = \Sigma(|F_o - |F_c|)/\Sigma|F_o|$ $\quad$ $^b R_w(F_o) = \Sigma(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$, $w^{-1} = \sigma^2(F_o) + gF_o^2$

with anisotropic thermal parameters, and all hydrogen atoms were idealized. Atomic coordinates are given in Tables 2 and 3, and selected bond distances and angles in Table 4. All computations used the SHELXTL PLUS (Version 4.21, 1990) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Results and discussion

The reaction of $[Ru(CO)_2X_2]_n$ (X = Cl, Br, I) with APT in boiling methanol yields the corresponding $Ru(CO)_2X_2(APT)$ complexes (**I**). ^1H NMR, IR and microanalysis data support this formulation for **I**. An NMR peak at about 3.16 ppm, together with analytical data, indicate that **I** (X = Cl, Br) crystallizes from methanol with one solvent molecule. A similar reaction between $Re(CO)_5Cl$ and APT in toluene yields a yellow product which has been similarly characterized and formulated as $Re(CO)_3Cl(APT)$ (**II**). Complex **I** (X = Cl) crystallizes in two forms, an orange form and a yellow form. Based on spectroscopic and analytical data both forms have the formulation $Ru(CO)_2Cl_2(APT)\cdot CH_3OH$ and are most likely examples of linkage isomerism in which the APT ligand coordinates in the **A** and **B** bidentate configurations. From crystallographic data on **IA**(Cl), in which no CH_3OH was found, it can be concluded that both solvated and unsolvated crystalline forms exist with the solvated form dominating but of lower crystal quality. Bidentate coordination of APT might be expected since previous studies have shown that the reaction of $[Ru(CO)_2X_2]_n$ with ligands that are usually tridentate, such as 2,2′:6′,2″-terpyridine (tpy) [8] and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPT) [9], yields octahedral $Ru(CO)_2X_2(tpy)$ and $(\mu\text{-TPT})[Ru(CO)_2X_2]_2$ complexes, respectively, in which the tpy and TPT function as bidentate ligands. Similar bidentate coordination has also been observed for $Re(CO)_3Cl(tpy)$ [10]. In all of these complexes the CO and halogen ligands are not readily displaced as indicated by the failure of the free pyridyl rings to coordinate. Configuration **A** involves coordination through the pyridyl and triazole groups, while in configuration **B** coordination occurs through the pyridyl and amino groups. the major difference in the NMR spectra for the two forms of **I** is the chemical shift of the amino protons. For the orange isomer, the amino protons appear as a singlet at 7.51 ppm (compared to 7.83 ppm for the free ligand), whereas for the yellow isomer this peak is shifted downfield to 10.7 ppm. This suggests configuration **A**

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **IA**(Cl)

	x	*y*	*z*	U_{eq}[a]
Ru	7914(1)	1164(1)	1980(1)	40(1)
Cl(1)	8131(1)	1573(1)	260(1)	47(1)
Cl(2)	7743(1)	615(1)	3633(1)	66(1)
O(1)	6310(3)	2100(3)	2239(4)	90(2)
O(2)	9032(3)	2371(3)	2936(4)	98(2)
N(1)	8921(3)	352(2)	1662(3)	42(1)
N(2)	7322(2)	235(2)	1448(3)	39(1)
N(3)	7149(3)	−937(2)	1027(3)	40(1)
N(4)	7421(3)	−1657(2)	670(4)	53(2)
N(5)	5606(3)	−1804(3)	770(4)	64(2)
N(6)	6361(2)	67(2)	1356(3)	38(1)
C(1)	6934(4)	1762(3)	2145(4)	55(2)
C(2)	8629(4)	1919(3)	2547(5)	59(2)
C(3)	9785(3)	472(3)	1722(4)	53(2)
C(4)	10383(3)	−89(4)	1451(4)	58(2)
C(5)	10098(4)	−776(4)	1169(5)	61(2)
C(6)	9220(3)	−914(3)	1105(4)	55(2)
C(7)	8644(3)	−337(3)	1339(4)	39(2)
C(8)	7699(3)	−374(3)	1262(4)	39(2)
C(9)	6325(3)	−647(3)	1091(3)	35(2)
C(10)	5515(3)	−1057(3)	919(4)	41(2)
C(11)	4722(3)	−704(3)	927(4)	48(2)
C(12)	3981(3)	−1125(3)	761(5)	56(2)
C(13)	4061(4)	−1886(4)	580(5)	71(3)
C(14)	4876(4)	−2200(3)	581(6)	80(3)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **IB**(Cl)

	x	*y*	*z*	U_{eq}[a]
Ru	7975.6(2)	7731.5(7)	1244.8(1)	31.4(1)
Cl(1)	5710.4(7)	8275.1(7)	2637.1(5)	45.2(2)
Cl(2)	10341.9(8)	7062.1(7)	−49.1(5)	45.1(2)
O(1)	6120(3)	6354(3)	−88(2)	71(1)
O(2)	6555(3)	10603(2)	82(2)	64(1)
O(3)	7797(3)	4976(3)	7447(2)	64(1)
N(1)	9353(2)	8627(2)	2250(2)	35(1)
N(2)	8492(3)	6877(2)	4917(2)	43(1)
N(3)	8644(2)	5917(2)	3314(1)	33(1)
N(4)	8980(2)	5731(2)	2150(1)	34(1)
N(5)	7414(3)	3609(2)	2803(2)	47(1)
N(6)	7870(3)	5691(2)	5080(2)	43(1)
C(1)	6841(3)	6859(3)	405(2)	44(1)
C(2)	7121(3)	9519(3)	512(2)	42(1)
C(3)	9993(3)	9699(3)	1802(2)	43(1)
C(4)	10861(3)	10373(3)	2367(2)	51(1)
C(5)	11122(3)	9914(3)	3439(2)	51(1)
C(6)	10478(3)	8794(3)	3918(2)	46(1)
C(7)	9603(3)	8181(2)	3312(2)	35(1)
C(8)	8928(3)	7009(2)	3845(2)	36(1)
C(9)	7936(3)	5130(2)	4102(2)	36(1)
C(10)	7255(3)	3947(2)	3873(2)	38(1)
C(11)	6444(3)	3268(3)	4712(2)	50(1)
C(12)	5811(4)	2175(3)	4426(3)	62(1)
C(13)	5968(4)	1824(3)	3329(3)	65(1)
C(14)	6786(4)	2583(3)	2534(3)	59(1)
C(15)	6689(4)	4181(4)	7880(3)	59(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 4 Selected bond distances and angles for **IA**(Cl) and **IB**(Cl) CH_3OH

	IA(Cl)	**IB**(Cl) CH_3OH
Bond distances (Å)		
Ru–Cl(1)	2.387(1)	2.394(1)
Ru–Cl(2)	2.386(1)	3.391(1)
Ru–C(1)	1.851(6)	1.877(4)
Ru–C(2)	1.881(6)	1.870(4)
Ru–N(1)	2.150(4)	2.174(3)
Ru–N(2)	2.070(4)	
Ru–N(4)		2.152(2)
C(1)–O(1)	1.135(8)	1.133(4)
C(2)–O(2)	1 131(8)	1.136(4)
N(3)–N(4)	1.422(6)	1.419(3)
Bond angles (°)		
Cl(1)–Ru–Cl(2)	173.4(1)	175.8(1)
Cl(1)–Ru–C(1)	92.8(2)	89 8(1)
Cl(1)–Ru–C(2)	94.3(2)	89.3(1)
Cl(1)–Ru–N(1)	85.5(1)	90 7(1)
Cl(1)–Ru–N(2)	89 7(1)	
Cl(1)–Ru–N(4)		89.8(1)
Cl(2)–Ru–C(1)	92.2(2)	91 8(1)
Cl(2)–Ru–C(2)	89.8(2)	94 7(2)
Cl(2)–Ru–N(1)	88.9(1)	87.6(1)
Cl(2)–Ru–N(2)	85.7(1)	
Cl(2)–Ru–N(4)		86 2(1)
C(1)–Ru–C(2)	91 2(3)	88 5(1)
C(1)–Ru–N(1)	171 1(2)	177 0(2)
C(1)–Ru–N(2)	94 9(2)	
C(1)–Ru–N(4)		94 0(2)
C(2)–Ru–N(1)	97 6(2)	94 5(1)
C(2)–Ru–N(2)	172 6(2)	
C(2)–Ru–N(4)		177 3(1)
N(1)–Ru–N(2)	76 4(1)	
N(1)–Ru–N(4)		83 0(1)

for the orange isomer (**IA**) and configuration **B** for the yellow isomer (**IB**). NMR assignments for all protons are given in 'Experimental'.

The bromo complex $Ru(CO)_2Br_2(APT)$ forms predominantly the yellow isomer and has a similar NMR spectrum to **IB** (X = Cl). A very small amount (<5%) of an orange isomer initially precipitates from the reaction mixture but is removed upon recrystallization. The iodo complex $Ru(CO)_2I_2(APT)$ crystallizes only as the orange isomer and has an NMR spectrum very similar to **IA** (X = Cl). The rhenium complex **II** also crystallizes in one form having an NMR similar to **IA** (X = Cl). Coordination directly to the less sterically crowded triazole ring, rather than the amino group, is preferred for the larger halogen ligands. For similar reasons, the larger radius of rhenium over ruthenium leads to adoption of configuration **A** for **II**.

X-ray crystal structures of **IA**(Cl) and **IB**(Cl)·MeOH were obtained. These structures are of unusual interest as they are coordination isomers of the ambidentate APT ligand. Both compounds crystallize as discrete, well separated molecules. Selected bond distances and angles for both structures are given in Table 4; drawings are given in Figs. 1 and 2. Both structures contain octahedrally coordinated Ru atoms. In both the Cl ligands are *trans* and the carbonyl and N donors are *cis*. In **IA**, in which Ru is coordinated to pyridyl and triazole N atoms, the angular deviations from octahedral symmetry are greater (4.8° average deviation in **IA**, compared to 2.9° in **IB**) than found in **IB**, in which Ru is coordinated to pyridyl and amino N atoms. This arises from the greater strain imposed by the five-membered chelate ring in **IA**, than by the six-membered ring in **IB**. The effect is most conspicuous in the N–Ru–N bond angles: in **IA**, N(1)–Ru–N(2) is 76.4(1)°, while in **IB**, N(1)–Ru–N(4) is relaxed to 83.0(1)°.

The three prior structures of complexes containing the APT ligand [3–5] are all similar to **IA** in the choice of N atoms for coordination; **IB**, therefore, represents

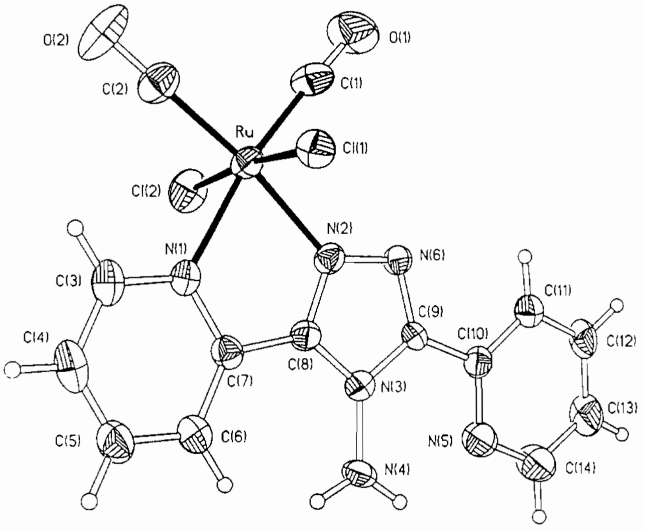


Fig. 1. The molecular structure of **IA**(Cl) drawn with 35% thermal ellipsoids

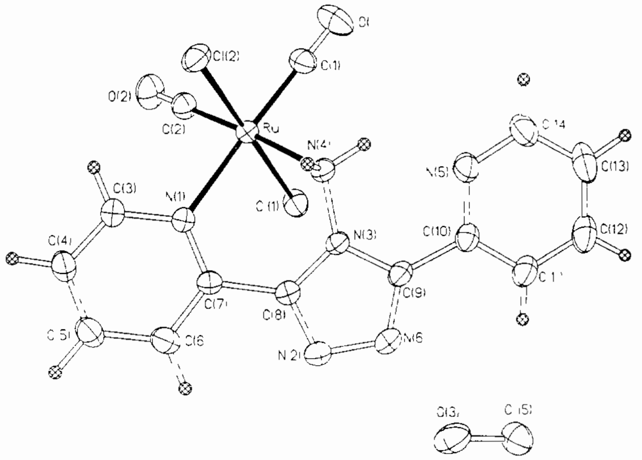


Fig. 2 The molecular structure **IB**(Cl) MeOH drawn with 35% thermal ellipsoids The solvent molecule is shown in its appropriate lattice position

the first structurally characterized example of **B** mode coordination. The greatest difference in the structural parameters of the APT ligand in the two coordination modes is in the dihedral angles between the ligand rings. In the previous structures, only small ($<10°$) dihedral angles have been observed; **IA** is in agreement (the coordinated pyridyl ring and the triazole ring are related by a 3.9° dihedral angle, and the uncoordinated ring by a 5.5° dihedral angle). However, for the coordination isomer, **IB**, the coordinated pyridyl and triazole rings are related by a 28.8° dihedral angle. This twisting is required to optimize the chelate ring geometry and reveals that the barrier to rotation may not be as great as others have assumed in describing the earlier structures.

Acknowledgements

This work was supported in part by the AUM Grant-in-Aid program and by the donors of the Petroleum Research Fund administered by the American Chemical Society.

References

1 N C. Thomas and J. Fischer, *J. Coord Chem, 21* (1990) 119.
2 F. Dallacker, *Monatsh. Chem., 91* (1960) 294.
3 F.S. Keij, R.A.G. de Graaff, J G. Haasnoot and J. Reedijk, *J Chem Soc, Dalton Trans,* (1984) 2093.
4 M.P. Garcia, J.A. Manero, L.A Oro, M.C Apreda, F.H. Cano, C Foces-Foces, J.G. Haasnoot, R. Prins and J Reedijk, *Inorg Chim Acta, 122* (1986) 235.
5 C Faulmann, P.J. van Koningsbruggen, R.A G. de Graff, J.G Haasnoot and J. Reedijk, *Acta Crystallogr, Sect C, 46* (1990) 2357
6 J.P. Cornelissen, J H. van Dieman, L R Groenovelt, J.G Haasnoot, A.L Spek and J. Reedijk, *Inorg Chem, 31* (1992) 198.
7 M J. Cleare and W.P Griffith, *J Chem Soc A,* (1969) 372.
8 G B. Deacon, J.M. Patrick, B W. Skelton, N.C. Thomas and A H. White, *Aust. J. Chem, 37* (1984) 929.
9 N C. Thomas, B.L. Foley and A.L. Rheingold, *Inorg Chem, 27* (1988) 3426.
10 P.A. Anderson, F.R. Keene, E. Horn and E.R.T. Tiekink, *Appl Organomet Chem, 4* (1990) 523.