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Complexes of 2-(Phenylazo)pyridine. Chemical Reactivity and Crystal and Molecular Structure of Conformers of $[Ru(azpy)_2(N_3)_2]$ *

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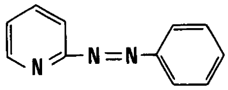
$[Ru\,azpy_2(N_3)_2]$ (azpy=2-(phenylazo)pyridine), $[Ru(C_{11}H_9N_3)_2(N_3)_2]$, crystallizes in the monoclinic system, space group *Cc* with a=12.739(2) Å, b=17.092(2) Å, c=21.759(4) Å, β=91.39(2)° and Z=8. The structure was solved and refined from diffractometer data to an R-value of 0.031 for the 3153 contributing reflections. Coordination around the two crystallographically independent complexes is almost identical, the main difference being different conformations of one phenyl and one azide group. Pyridine nitrogens are trans; average Ru–N bond lengths [pyridine N, 2.035(6) Å, azo N, 1.975(6) Å, azide N, 2.114(7) Å] indicate substantial Ru back π-bonding to azpy.

The complex contains reactive azido-groups. Treatment of this isomer with HCl in acetone rapidly yields only α-$[Ru(azpy)_2Cl_2]$. The other isomer of $[Ru(azpy)_2(N_3)_2]$ (separated chromatographically) yields only β-$[Ru(azpy)_2Cl_2]$; the reactions are stereoretentive under these mild conditions. Reaction with benzoyl chloride rapidly forms a new compound which then slowly forms $[Ru(azpy)_2Cl_2]$. Other reagents attack the azido-complex, the evidence indicating attack to be on the coordinated azido-group.

In recent years a remarkable number of reports have appeared on 2,2′-bipyridyl (bpy) complexes of ruthenium(II). The interest in these compounds stems from properties apparently fostered by the ligand's π-accepting ability leading to a pronounced metal to ligand "back π-bond".[2] Our interest in this general area led us to seek new, potentially π-accepting, ligands to extend the variety of such compounds and further probe the nature of bonding in such complexes. We found 2-(phenylazo)pyridine (azpy) (*1*) to be a very versatile ligand for such studies with ruthenium(II);[3,4] others have also reported such studies recently.[5–7]



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* See Ref. 1.

0302-4377/85 $2.50

During our synthetic studies we have developed several potential intermediates containing the "Ru(azpy)$_2$" unit. [Ru(azpy)$_2$(N$_3$)$_2$] could well be a synthetically useful compound because of the known chemical reactivity of the azide ion.[8] Questions arise regarding the reactivity of such a complex; does it undergo facile azide loss and are any of the reactions stereoretentive?

Several other questions arose during the course of our work with this ligand. Firstly, while we have considered the ligating atoms to be pyridine nitrogen and the azo-nitrogen adjacent to the phenyl ring,[3,4] no definite structural evidence was available. Nitrogen adjacent to pyridine or the azo-multiple bond could very well be ligators. Secondly, we earlier proposed the "Ru(azpy)$_2$" unit as an infrared π-bonding probe, and [Ru(azpy)$_2$(N$_3$)$_2$] was shown to have a strong Ru-azpy π-interaction.[4] Do structural data concur? And thirdly, which *cis*-configuration does our α-isomer have? Of the three possibilities one isomer (of C_1 symmetry) is the β-configuration. Of the remaining two (C_2 symmetry) one has *trans*-pyridines while the other has *trans*-azo-groups. Only one form is obtained in synthesis but until now its configuration was not known.

The present work was undertaken to answer these questions. We have examined some reactions of the coordinated azido groups, finding stereoretention, and a crystal structure of α-[Ru(azpy)$_2$(N$_3$)$_2$] supports our earlier conclusions based on infrared evidence. Furthermore, the structure turned out to be interesting because of the presence of two different molecular conformers, to our knowledge a rare example of such occurence in coordination compounds.

EXPERIMENTAL

Materials. Organic Solvents and reagents were used as received from Aldrich Chemical. [Ru(azpy)$_2$(N$_3$)$_2$] was prepared as reported earlier.[4] Silica gel 60 for column chromatography was from EM Reagents; precoated thin-layer chromatography plates were silica gel 60 with fluorescent indicator (aluminum backed).

Separation of [Ru(azpy)$_2$(N$_3$)$_2$] isomers. The isomeric mixture was dissolved in chloroform (200mg/50 ml) and loaded onto a silica gel column (*ca.* 15×400 mm) packed in chloroform. Development was with ethyl acetate-chloroform mixtures, starting with 10 % ethylacetate. The first fractions were evaporated, dissolved in chloroform and petroleum ether (low boiling) added to precipitate the product (α-configuration). The fractions of the other isomer (β-configuration) were evaporated to low volume and petroleum ether added. Isomeric purity was established by TLC (ethylacetate development).

Reactions. In the following reactions small quantities (5 mg) *have been used.* While no explosions occurred we feel it prudent to recommend caution.

Reaction with hydrochloric acid. The isomer of α-configuration of [Ru(azpy)$_2$(N$_3$)$_2$] was dissolved in acetone (5 mg in 5 ml) and 10 drops conc HCl added at room temperature; an immediate color change (blue to purple) was observed. In 30 min TLC of the solution showed none of the starting azido complex present. Only α-[Ru(azpy)$_2$Cl$_2$] and a small amount of a brown decomposition product at the TLC origin could be detected. Similar results were observed in hot acetone.

Mixing a hot chloroform solution of α-[Ru(azpy)$_2$(N$_3$)$_2$] with conc. HCl again gave only α-[Ru(azpy)$_2$Cl$_2$]. However, after 2½ h some β-[Ru(azpy)$_2$Cl$_2$] could be detected in this solvent.

Treating β-[Ru(azpy)$_2$(N$_3$)$_2$] in the same fashion led to the formation of β-[Ru(azpy)$_2$Cl$_2$] and again a small amount of a decomposition product at the TLC origin. None of the α-isomer could be detected after 3 days.

Reaction with benzoyl chloride. A solution of [Ru(azpy)$_2$(N$_3$)$_2$] in acetone (room temperature) was mixed with a few drops of benzoyl chloride. In 2 min TLC detected none of the azido starting complex; only a new substance was present at the TLC origin suggesting the presence of a complex cation. This material diminished over a 3 day period with the formation of $[Ru(azpy)_2Cl_2]$. In one experiment with pure β-$[Ru(azpy)_2(N_3)_2]$ only β-$[Ru(azpy)_2Cl_2]$ was formed, indicating retention of configuration.

Reaction with other reagents. General reactivity of the azido group was investigated by dissolving $[Ru(azpy)_2(N_3)_2]$ in a solvent with an added reagent and running TLC of the solution over a period of time. Reagents were: phenacyl chloride (in boiling toluene), giving a new component which slowly (*ca.* one day) converts to $[Ru(azpy)_2Cl_2]$. Phenylacetonitrile (neat, hot), complete loss of azido-complex in 1 h. Norbornylene (in boiling toluene) slowly forms new components but incomplete in 20 h. Dicyclopentadiene (in boiling toluene), complete loss of azido complex in $3\frac{1}{2}$ h. Dimethylacetylenedicarboxylate (in acetone), complete loss of azido complex in 2 h. No attempt has been made to characterize the products of these reactions.

Crystallography. The compound crystallizes as dark violet rhombic shaped plates, which were assigned to the monoclinic system on the basis of precession and Weissenberg photographs. The plate face is {001}. The systematically absent reflections hkl for $h+k=2n+1$ and $h0l$ for $l=2n$ are consistent with the space groups $C2/c$ or Cc.

Diffraction data were obtained from a single crystal with the dimensions 0.45×0.22×0.08 mm. The data were collected at 296 K with an Enraf-Nonius CAD-4 diffractometer using Mo$K\alpha$ radiation monochromatized from highly mosaic graphite crystal. To investigate if the single crystal data are representative for the sample, the powder diffraction pattern was also recorded. All the lines in this pattern were easily indexed on basis of the single crystal cell constants. The crystal data and other information pertinent to data collection and refinement are given in Table 1. The diffractometer was operated in the $\omega-\theta$ scan mode. Intensities of four standard reflections measured after every 10800 s during the data collection showed no significant variations. Data processing included corrections for Lorentz, polarization and background effects but no correction for absorption. The symmetry related reflections were averaged; standard deviations for the measured intensities were based on counting statistics.

Table 1. Crystal data.

Space group	Cc, monoclinic
Cell constants	
a Å	12.739(2)
b Å	17.092(2)
c Å	21.759(4)
β°	91.39(2)
V Å^3	4736
Molecular formula	$RuC_{22}N_{12}H_{18}$
Molecular weight	551.5
Molecules/cell	$Z=8$
Calculated density (g/cm^3)	1.54
Observed density (g/cm^3)	1.50
Linear absorption coefficient (cm^{-1}), μ	6.82
Radiation (Mo$K\alpha$) (Å), λ	0.71073
Collection range ($h,k\pm l$) (°)	$1.85\leq\theta\leq25.50$
Scan width, $\Delta\theta$	$1.00+0.350\cdot\tan\theta$
Max scan time (s)	180
Maximum requested $\sigma(I)/I$	0.01
Scan speed range (°)	0.6−6.7
Number of independent reflections collected	4262
Independent data With $I/\sigma(I)\geq2.0$	3153
Number of variables	454
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.031
$R_w=\{\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2\}^{\frac{1}{2}}$	0.034

Table 2. Positional parameters and isotropic thermal parameters in units of Å^2 for the two conformers of [Ru(azpy)$_2$ (N$_3$)$_2$].

Atom	*x*	*y*	*z*	U_{iso}
Ru1	0.21884	0.05435(5)	0.39849	0.0441
N10	0.3505(6)	0.0078(5)	0.3630(4)	0.069
N11	0.3522(6)	−0.0299(4)	0.3126(4)	0.067
N12	0.3556(10)	−0.0528(6)	0.2639(5)	0.125
N110	0.2378(5)	0.0036(4)	0.4834(3)	0.048(2)
C111	0.3068(7)	−0.0523(5)	0.5023(4)	0.065(2)
C112	0.3181(8)	−0.0726(5)	0.5639(5)	0.075
C113	0.2615(8)	−0.0331(6)	0.6068(5)	0.070
C114	0.1930(7)	0.0228(6)	0.5887(4)	0.064
C115	0.1832(6)	0.0405(4)	0.5262(3)	0.046(2)
N1	0.1121(5)	0.0973(4)	0.5061(3)	0.049(2)
N120	0.1150(5)	0.1059(3)	0.4474(3)	0.0406(14)
C121	0.0397(6)	0.1633(5)	0.4239(3)	0.047(2)
C122	−0.0487(8)	0.1364(5)	0.3923(4)	0.061(2)
C123	−0.1208(8)	0.1906(6)	0.3691(5)	0.075
C124	−0.1028(9)	0.2682(6)	0.3780(5)	0.078
C125	−0.0122(8)	0.2929(5)	0.4080(5)	0.079
C126	0.0585(7)	0.2397(5)	0.4317(4)	0.058(2)
N20	0.3290(6)	0.1373(4)	0.4292(4)	0.061
N21	0.4088(6)	0.1165(5)	0.4523(3)	0.064
N22	0.4875(8)	0.1013(6)	0.4755(5)	0.100
N210	0.1882(5)	0.1173(4)	0.3208(3)	0.054(2)
C211	0.2165(8)	0.1926(6)	0.3101(5)	0.062(3)
C212	0.1818(9)	0.2320(6)	0.2589(6)	0.083
C213	0.1162(9)	0.1945(7)	0.2165(5)	0.085
C214	0.0877(8)	0.1178(6)	0.2272(4)	0.074
C215	0.1261(7)	0.0815(5)	0.2805(4)	0.058(2)
N2	0.0997(6)	0.0062(4)	0.2911(3)	0.060(2)
N220	0.1307(5)	−0.0183(4)	0.3449(3)	0.050(2)
C221	0.1166(7)	−0.1001(5)	0.3648(4)	0.057(2)
C222	0.0974(8)	−0.1283(6)	0.4113(4)	0.067(2)
C223	0.0778(9)	−0.2084(7)	0.4196(5)	0.081(3)
C224	0.0886(10)	−0.2572(6)	0.3719(6)	0.093
C225	0.1100(10)	−0.2309(7)	0.3150(6)	0.095
C226	0.1217(8)	−0.1515(6)	0.3045(5)	0.072
Ru2	0.29106(5)	0.55527(4)	0.09929(3)	0.0344
N30	0.4536(5)	0.5482(3)	0.0811(3)	0.054
N31	0.5045(5)	0.6040(4)	0.0740(3)	0.043
N32	0.5585(7)	0.6551(5)	0.0669(5)	0.098
N310	0.2716(4)	0.4432(3)	0.0714(2)	0.0374(12)
C311	0.3405(6)	0.3969(4)	0.0438(3)	0.044(2)
C312	0.3195(6)	0.3177(4)	0.0345(4)	0.051(2)
C313	0.2260(6)	0.2878(5)	0.0534(4)	0.054(2)
C314	0.1548(6)	0.3352(5)	0.0806(4)	0.050(2)
C315	0.1791(5)	0.4133(4)	0.0896(3)	0.038(2)
N3	0.1085(5)	0.4637(4)	0.1149(3)	0.046(2)
N320	0.1447(5)	0.5341(4)	0.1178(3)	0.041(2)
C321	0.0729(6)	0.5899(5)	0.1438(4)	0.047(2)
C322	0.0686(7)	0.6649(5)	0.1193(4)	0.054(2)
C323	0.0018(7)	0.7187(5)	0.1453(5)	0.069
C324	−0.0549(7)	0.6989(6)	0.1945(6)	0.076
C325	−0.0496(8)	0.6262(6)	0.2189(5)	0.079
C326	0.0135(7)	0.5703(5)	0.1939(4)	0.059(2)

N40	0.3329(6)	0.5124(4)	0.1868(3)	0.054
N41	0.3657(7)	0.4497(5)	0.1939(3)	0.073
N42	0.4022(12)	0.3888(6)	0.2023(5)	0.158
N410	0.3122(4)	0.6676(3)	0.1282(2)	0.0404(13)
C411	0.3267(7)	0.6937(5)	0.1854(4)	0.047(2)
C412	0.3486(8)	0.7727(5)	0.1968(4)	0.065
C413	0.3558(8)	0.8237(5)	0.1486(5)	0.067
C414	0.3407(7)	0.7964(4)	0.0905(5)	0.062
C415	0.3185(6)	0.7185(4)	0.0807(3)	0.048(2)
N4	0.2988(5)	0.6908(4)	0.0224(3)	0.050(2)
N420	0.2753(5)	0.6174(3)	0.0222(3)	0.0403(14)
C421	0.2576(6)	0.5864(5)	−0.0388(3)	0.047(2)
C422	0.1803(7)	0.5318(5)	−0.0494(4)	0.059(2)
C423	0.1625(9)	0.5039(6)	−0.1079(5)	0.079
C424	0.2242(12)	0.5291(7)	−0.1555(5)	0.102
C425	0.3015(10)	0.5839(8)	−0.1446(5)	0.092
C426	0.3180(8)	0.6134(6)	−0.0861(4)	0.072(3)

[a] For the atoms refined with anisotropic thermal parameters $U_{iso}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^* \cdot a_j^* \cdot \bar{a}_i \cdot \bar{a}_j$.

Structure solution and refinement. The Patterson map clearly indicated the positions of the Ru atoms corresponding to one generally placed Ru atom per asymmetric unit in the space group *C2/c*. A structure factor calculation based on these positions gave an R-value of 0.23. However, numerous attemps to solve the structure in the space group *C2/c* were all fruitless. The intensity statistics did not clearly indicate whether the structure is centric or acentric.

Progress in the structure determination was finally achieved when the results from a DIRDIF[9] run were combined with the information from Ru-phased difference density assuming that the space group symmetry is *Cc*. The two independent Ru atoms are related by symmetry corresponding to *C2/c*. In this way seven of the twelve coordinating nitrogen atoms were localized and the corresponding R-value dropped to 0.207. The structure was refined by full matrix least squares minimizing $\Sigma\omega(|F_o|-|F_c|)^2$. After ten successive least squares iterations and difference density calculations, the 70 non-hydrogen atoms in the structure were all located; when isotropic refinement had converged the corresponding unit weighted residual was 0.060. Due to the limited number of data anisotropic temperature factors were only introduced for the atoms where the difference density indicated that it would improve the refinement model. The positions for the hydrogen atoms were also found in the difference density. The contribution from the hydrogen atoms was included in the refinement but their parameters were not refined. Their positions were fixed at the idealized positions and they were given a common isotropic thermal parameter (U=0.045 Å^2). The opposite enantiomer of the crystal could be rejected at a significance level less than 10^{-6} by Hamiltons R-value test performed as described by Rogers.[10]

In the final cycles of least squares 35 atoms were refined anisotropically and the weights were changed from unit weights to weights of the form $\omega^{-1}=\sigma^2(F)+0.0003|F|^2$. After the final refinement cycle the maximum shift for the parameters was 0.03 σ and the largest peaks in the difference density of a height of 0.4 e/ Å^3 were found close to the Ru atoms. The final residuals are R=0.031 and R_ω=0.034. An inspection of the data showed that these do not suffer from extinction.

The atomic scattering factors used in the calculations were by Cromer and Mann[11] using the values for the neutral atoms, except for hydrogen, where the values by Stewart *et al.*[12] were used. The anomalous scattering corrections added to the scattering factor for Ru were calculated by Cromer and Liberman.[13]

The positional parameters with standard deviations derived from the final cycle of least squares are listed in Table 2. Thermal parameters and a table of observed and calculated structure amplitudes are available from the authors. The computer programs employed in this work were the X-Ray system[14] for the crystallographic computations and ORTEP II[15] for the illustrations.

RESULTS AND DISCUSSION

Chemical characterization. [Ru(azpy)$_2$(N$_3$)$_2$] is synthesized as a mixture of two isomers, readily separated by thin layer chromatography. These isomers have the same geometric structure as the cis α- and β-isomers of [Ru(azpy)$_2$Cl$_2$].[3] We earlier reached this conclusion from a line of chemical reasoning; [Ru(azpy)$_2$(NO$_2$)$_2$] (as two isomers) or the aquo complex prepared from it react with hydrochloric acid to produce only α- and β-[Ru(azpy)$_2$Cl$_2$] and none of the less stable[3] *trans*-dichloro complex (γ-isomer). The azido complex, produced from the aquo compound, consists of two isomers reasonably expected to have the geometry of the α- and β-dichloro complexes. In the present work this is shown to be the case.

Reactions of Ru-azpy compounds have received a little attention. Chakravorty's group[7] reports that chloride removal from [Ru(azpy)$_2$Cl$_2$] by silver ion is stereoretentive, but our own work suggests otherwise. This discrepancy is most likely a matter of definition. The former conclusion was reached using NMR on complexes of the methyl substituted ligand, while our own conclusion is based on the very sensitive thin layer chromatographic (TLC) technique. A further example of the sensitivity of TLC is that an X-ray powder photograph on a representative sample of the α-complex shows only one isomer in [Ru(azpy)$_2$(N$_3$)$_2$]. This establishes the other form to be present in less than *ca.* 10 %. On the other hand TLC clearly detects two isomers, one in lesser amount than the second. It would appear that the TLC technique is capable of detecting very small quantities in these systems.

In view of the lack of stereoretention in reaction of both [Ru(azpy)$_2$(NO$_2$)$_2$][4] and [Ru(azpy)$_2$Cl$_2$] it was of interest to examine [Ru(azpy)$_2$(N$_3$)$_2$] in this regard, particularly since many of the reactions of this latter compound occur at ambient temperature. We found that [Ru(azpy)$_2$(N$_3$)$_2$] in acetone solution reacts rapidly at room temperature with aqueous hydrochloric acid. Starting with pure α-isomer (the structure of which is reported here) the only dichloro complex is α-[Ru(azpy)$_2$Cl$_2$] (by TLC). Crystallographic evidence is claimed[7] to show the α-isomer having *cis*-chlorides, *cis*-azo groups, and *trans*-pyridine groups (*i.e.*, the azpy ligands disposed as in the present structure). Thus, this reaction of α-[Ru(azpy)$_2$(N$_3$)$_2$] is stereoretentive.

Under the same reaction conditions the other isomer of [Ru(azpy)$_2$(N$_3$)$_2$] gives exclusively β-[Ru(azpy)$_2$Cl$_2$] (TLC). While we do not know the structure of this azido-isomer, we do infer it to be geometrically the same as β-[Ru(azpy)$_2$Cl$_2$] from the evidence cited above. Again, the reaction appears to be stereoretentive for this isomer as well.

Reactions of [Ru(azpy)$_2$(N$_3$)$_2$] are not necessarily simple substitution but may, in many situations, involve direct attack on azido-ligands. For example, reaction with benzoyl chloride in acetone solution rapidly (minutes at room temperature) leads to a new (unidentified) compound. This slowly (several days) forms [Ru(azpy)$_2$Cl$_2$], with retention of configuration observed for one isomer. We presume the intermediate to be a benzoyl azide complex rather than a solvate. If the intermediate was an acetone complex its reaction with chloride ion (liberated by the benzoyl chloride) should be nearly as rapid as observed with hydrochloric acid.

Further support for attack on coordinated azido-groups is gained in the reaction with phenacyl chloride in hot toluene. Here no solvent intermediate is anticipated. Again we observe the formation of a new compound (TLC) which then slowly forms [Ru(azpy)$_2$Cl$_2$].

A number of other reagents, expected to attack azide ion or azido-groups,[8] do indeed react with [Ru(azpy)$_2$(N$_3$)$_2$]. These observations are described in the experimental section; the reagents used suggest the wide variety of reactions possible.

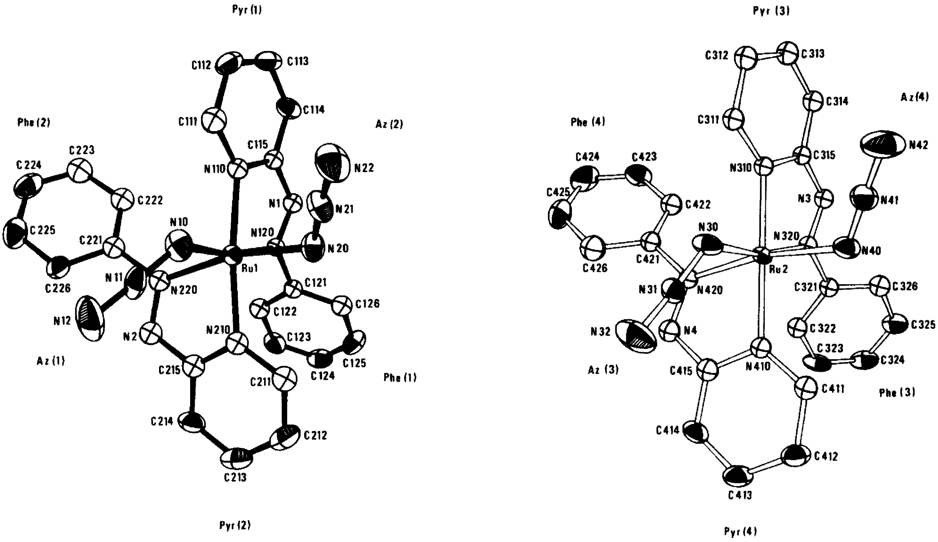


Fig. 1. Perspective views of the conformers, I and II of [Ru(azpy)$_2$(N$_3$)$_2$] showing the labelling of the atoms and the ligands. Conformer II is drawn with the open bonds in this figure and in Fig. 2. The thermal ellipsoids are drawn at the 50 % probability level. The atoms drawn as open "foot balls" are those refined with anisotropic thermal parameters.

Description and discussion of the structure. A very remarkable feature in this structure is that it contains two different conformers of the same complex. The molecular geometry and stereochemistry is illustrated by the lists of bond lengths and angles given in Tables 3 and 4 and by Fig. 1, which shows the two crystallographically independent complexes seen in the same orientation with the atomic labelling. The most significant difference between the two ruthenium complexes is in the orientation of the phenyl and the azido groups.

To describe these small variations, least squares planes have been calculated for pyridine and phenyl rings and for the planes defined by Ru and the coordinated azide ions; these units are all planar within the experimental uncertainty. In Table 5 the interplanar angles between these least squares planes are given for the two conformers. An inspection of this Table reveals that the two equivalent phenyl groups phe(1) and phe(3) are in different orientations in the two conformers. Similarly, the azido groups az(1) and az(3) are also oriented differently. The other differences are much smaller and hardly significant. All intermolecular contacts less than 4 Å have been investigated to see if the crystal packing causes the difference in conformation of the molecules. A number of interatomic distances are close to the sum of the van der Waals radii[16] of the atoms involved ($d_{\mathrm{vdw}}(\mathrm{C-N})=3.25$ Å, $d_{\mathrm{vdw}}(\mathrm{C-C})=3.40$ Å). The shortest are from azide nitrogens to carbon atoms (Cj13 and Cj14) in the pyridine rings. The distance between N32 and C313($\frac{1}{2}+x,\frac{1}{2}+y,z$)=3.13 Å represents the minimum value.

The contact distances between the carbon atoms of the phenyl- and pyridine rings are slightly longer than the sum of the van der Waals radii. (3.5–3.9 Å). These interactions and inspection of the crystal packing, illustrated by the stereo pair in Fig. 2 makes it likely that other orientations of the phenyl – and azide groups could lead to an energetically less favourable packing.

The four independent azpy ligands are very similar and since complete crystallographic

Table 3. Bond lengths (Å) in the two conformers I and II.

I		II	
Ru1–N110	2.050(6)	Ru2–N310	2.023(6)
Ru1–N210	2.032(7)	Ru2–N410	2.036(6)
Ru1–N120	1.931(6)	Ru2–N320	1.951(6)
Ru1–N220	2.029(7)	Ru2–N420	1.990(6)
Ru1–N10	2.146(8)	Ru2–N30	2.121(6)
Ru1–N20	2.093(7)	Ru2–N40	2.096(7)
N110–C111	1.355(11)	N310–C311	1.335(10)
C111–C112	1.388(15)	C311–C312	1.394(11)
C112–C113	1.372(15)	C312–C313	1.369(11)
C113–C114	1.347(14)	C313–C314	1.361(11)
C114–C115	1.394(11)	C314–C315	1.384(11)
C115–N110	1.335(10)	C315–N310	1.352(9)
C115–N1	1.391(10)	C315–N3	1.371(10)
N1–N120	1.288(8)	N3–N320	1.289(9)
N120–C121	1.455(10)	N320–C321	1.445(10)
C121–C122	1.384(12)	C321–C322	1.388(12)
C122–C123	1.391(14)	C322–C323	1.384(13)
C123–C124	1.360(15)	C323–C324	1.349(16)
C124–C125	1.378(15)	C324–C325	1.353(15)
C125–C126	1.373(13)	C325–C326	1.371(13)
C126–C121	1.337(12)	C326–C321	1.384(12)
N210–C211	1.358(12)	N410–C411	1.331(10)
C211–C212	1.366(15)	C411–C412	1.400(12)
C212–C213	1.386(16)	C412–C413	1.367(13)
C213–C214	1.381(16)	C413–C414	1.358(14)
C214–C215	1.394(13)	C414–C415	1.375(11)
C215–N210	1.317(11)	C415–N410	1.355(10)
C215–N2	1.352(12)	C415–N4	1.370(10)
N2–N220	1.299(10)	N4–N420	1.291(9)
N220–C221	1.419(11)	N420–C421	1.443(10)
C221–C222	1.348(13)	C421–C422	1.372(12)
C222–C223	1.404(15)	C422–C423	1.373(14)
C223–C224	1.341(17)	C423–C424	1.382(17)
C224–C225	1.350(20)	C424–C425	1.375(20)
C225–C226	1.384(15)	C425–C426	1.381(14)
C226–C221	1.407(13)	C426–C421	1.378(13)
Azide groups			
N10–N11	1.159(13)	N30–N31	1.165(9)
N11–N12	1.133(15)	N31–N32	1.125(11)
N20–N21	1.178(11)	N40–N41	1.159(11)
N21–N22	1.142(13)	N41–N42	1.154(14)

details have not previously been reported for azpy as a ligand, we give some description here. In Fig. 3 the mean molecular geometry is illustrated and the atomic labelling is defined. The dihedral angles C*j*15–N*j*–N*j*20–C*j*21 (*j*=1,4) are all very close to 180° (Table 4) showing that the azo-group is almost coplanar with the pyridine ring. This is consistent with the fact that the C*j*15–N*j* distance (to the pyridine ring) is slightly shorter (1.378 Å) than the N*j*20–C*j*20 (phenyl ring) distance (1.441 Å). Our earlier work, suggesting

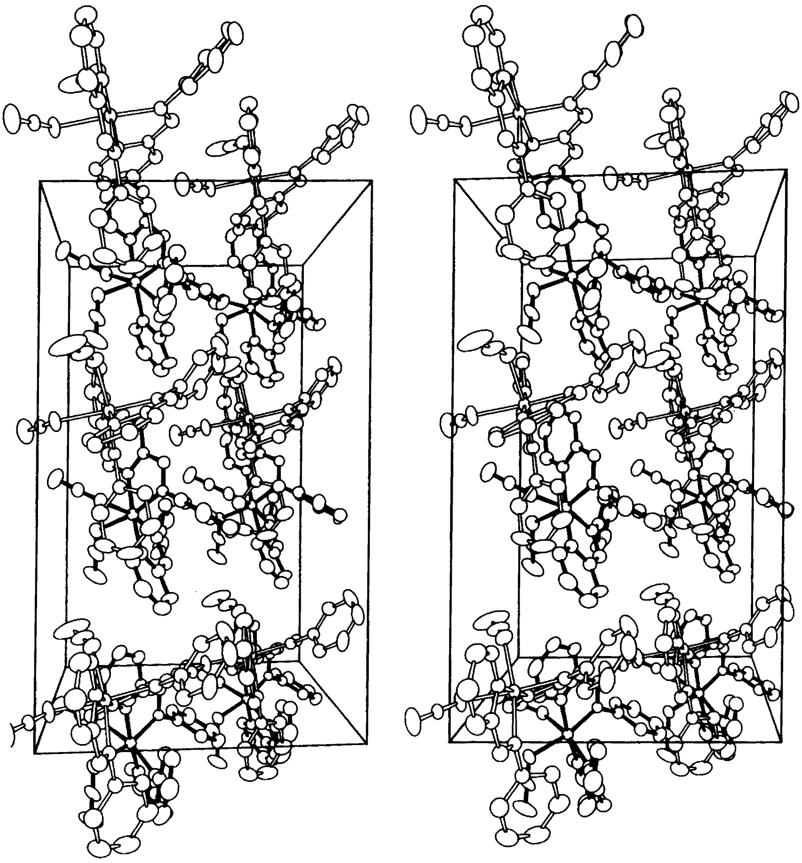
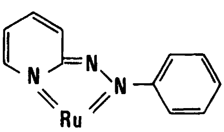


Fig. 2. Stereoscopic view of the packing in the unit cell of [Ru(azpy)$_2$(N$_3$)$_2$].

pronounced Ru-azo-multiple bonding and a lowering of the azo-bond order, also requires some increase in the C*j*15−N*j* bond order, this suggesting a prominent resonance form in the complex to be:



The other bond distances in azpy are normal.

The drawings and the bond distances show that the ligating atoms on azpy are the pyridine nitrogen (N*j*10) and azo-nitrogen (N*j*20), as considered to be the case earlier.[3,4] In Table 6 the results obtained from other structure determinations are compared. Some conclusions regarding bonding details are possible. In Ru bpy$_3^{2+}$ the Ru−N distance of 2.056 Å[17] is shorter than the same parameter in ruthenium(III)-bpy complexes (*ca.* 2.077 Å[18]); from this one readily concludes π-bonding in Ru bpy$_3^{2+}$ to be substantial. With no π-interaction a ruthenium(II)−nitrogen distance near 2.13 Å could be expected (complexes

Table 4. Bond angles and dihedral angles (deg) for the two conformers I and II of $[Ru(azpy)_2(N_3)_2]$.

I		II	
N110–Ru1–N10	92.2(3)	N310–Ru2–N30	90.2(3)
N110–Ru1–N20	86.3(3)	N310–Ru2–N40	88.2(3)
N110–Ru1–N220	108.0(3)	N310–Ru2–N420	104.0(3)
N110–Ru1–N120	76.4(3)	N310–Ru2–N320	77.1(3)
N120–Ru1–N20	88.7(3)	N320–Ru2–N40	88.3(3)
N120–Ru1–N10	167.7(2)	N320–Ru2–N30	166.0(3)
N210–Ru1–N20	91.2(3)	N410–Ru2–N40	91.2(3)
N210–Ru1–N10	95.7(3)	N410–Ru2–N30	89.4(3)
N210–Ru1–N120	95.5(3)	N410–Ru2–N320	103.3(2)
N210–Ru1–N220	75.9(3)	N410–Ru2–N420	76.5(2)
N220–Ru1–N10	85.1(3)	N420–Ru2–N30	87.3(3)
N220–Ru1–N20	163.3(3)	N420–Ru2–N40	165.8(3)
N120–Ru1–N220	102.8(3)	N320–Ru2–N420	101.3(2)
N10–Ru1–N20	85.8(3)	N30–Ru2–N40	85.5(3)
N110–Ru1–N210	171.5(2)	N310–Ru2–N410	179.3(11)
Ru1–N110–C111	129.3(6)	Ru2–N310–C311	128.3(5)
Ru1–N110–C115	112.1(5)	Ru2–N310–C315	111.7(4)
Ru1–N120–N1	122.1(5)	Ru2–N320–N3	120.3(5)
Ru1–N120–C121	124.7(5)	Ru2–N320–C321	125.1(5)
Ru1–N210–C211	126.7(6)	Ru2–N410–C411	128.2(5)
Ru1–N210–C215	114.1(6)	Ru2–N410–C415	112.4(5)
Ru1–N220–N2	117.9(5)	Ru2–N420–N4	119.8(5)
Ru1–N220–C221	125.9(5)	Ru2–N420–C421	126.2(5)
azpy (1)		*azpy (2)*	
C115–N110–C111	117.8(7)	C315–N310–C311	119.7(6)
N110–C111–C112	121.4(8)	N310–C311–C312	121.1(7)
C111–C112–C113	119.4(8)	C311–C312–C313	118.9(7)
C112–C113–C114	119.8(9)	C312–C313–C314	120.2(8)
C113–C114–C115	118.8(8)	C313–C314–C315	119.1(7)
C114–C115–N110	112.8(7)	C314–C315–N310	121.1(7)
C114–C115–N1	120.1(7)	C314–C315–N3	121.1(7)
N110–C115–N1	117.2(6)	N310–C315–N3	117.8(6)
C115–N1–N120	111.0(6)	C315–N3–N320	111.7(6)
N1–N120–C121	113.0(6)	N3–N320–C321	114.0(6)
N120–C121–C122	118.2(7)	N320–C321–C322	118.6(7)
N120–C121–C126	119.9(7)	N320–C321–C326	120.7(7)
C121–C122–C123	118.8(9)	C321–C322–C323	118.4(8)
C112–C123–C124	119.4(9)	C322–C323–C324	120.3(8)
C123–C124–C125	120.2(10)	C323–C324–C325	121.3(10)
C124–C125–C126	120.6(9)	C324–C325–C326	120.5(10)
C125–C126–C121	119.1(8)	C325–C326–C321	118.8(8)
C126–C121–C122	121.9(8)	C326–C321–C322	120.6(8)

azpy(2)		*azpy(4)*	
C215-N210-C211	118.9(7)	C415-N410-C411	119.2(6)
N210-C211-C212	121.7(9)	N410-C411-C412	120.8(8)
C211-C212-C213	119.6(10)	C411-C412-C413	119.7(9)
C212-C213-C214	118.9(10)	C412-C413-C414	118.9(8)
C213-C214-C215	118.3(9)	C413-C414-C415	120.1(8)
C214-C215-N210	122.8(8)	C414-C415-N410	121.3(7)
C214-C215-N2	118.8(8)	C414-C415-N4	120.7(7)
N210-C215-N2	118.4(8)	N410-C415-N4	118.1(7)
C215-N2-N220	113.3(7)	C415-N4-N420	112.1(6)
N2-N220-C221	115.0(7)	N4-N420-C421	113.0(6)
N220-C221-C222	121.0(8)	N420-C421-C422	119.9(7)
N220-C221-C226	119.0(8)	N420-C421-N426	119.2(7)
C221-C222-C223	120.1(9)	C421-C422-C423	119.5(8)
C222-C223-C224	119.0(10)	C422-C423-C424	120.2(10)
C223-C224-C225	122.0(11)	C423-C424-C425	120.1(10)
C224-C225-C226	120.2(11)	C424-C425-C426	119.9(10)
C225-C226-C221	118.4(10)	C425-C426-C421	119.4(10)
C226-C221-C222	120.0(8)	C426-C421-C422	120.9(8)
AZIDE(1)		*AZIDE(3)*	
Ru1-N10-N11	122.3(7)	Ru2-N30-N31	121.8(5)
N10-N11-N12	178.0(11)	N30-N31-N32	176.0(9)
AZIDE(2)		*AZIDE(4)*	
Ru1-N20-N21	119.7(6)	Ru2-N40-N41	121.9(6)
N20-N21-N22	175.5(10)	N40-N41-N42	177.0(12)

Dihedral Angles

azpy(1)		*azpy(3)*	
C114-C115-N1-N120	179.3(7)	C314-C315-N3-N320	178.1(7)
N110-C115-N1-N120	-2.3(9)	N310-C315-N2-N320	-0.8(9)
C115-N1-N120-C121	178.3(6)	C315-N3-N320-C321	179.5(6)
N1-N120-C121-C122	-106.4(8)	N3-N320-C320-C322	142.6(7)
N1-N120-C121-C126	75.6(9)	N3-N320-C321-C326	40.5(10)
azpy(2)		*azpy(4)*	
C214-C215-N2-N220	-173.3(8)	C414-C415-N4-N420	-177.3(7)
N210-C215-N2-N220	7.6(11)	N410-C415-N4-N420	0.6(10)
C215-N2-N220-C221	-172.3(7)	C415-N4-N420-C421	-178.1(6)
N2-N220-C221-C222	-148.7(8)	N4-N420-C421-C422	-142.5(8)
N2-N220-C221-C226	30.7(11)	N4-N420-C421-C426	36.4(10)

with ammonia[19,20] and ethylenediamine[21]). As anticipated the distances for ruthenium(III) with these ligands are somewhat shorter.

In the present complex the average nitrogen(pyridine)-ruthenium distance is 2.035 Å, one of the shortest yet reported for this ligator. Thus, we conclude there to be a substantial π-interaction in this bond.

This also appears to be true of the ruthenium-azpy (azo nitrogen) linkage. The average bond distance of 1.975 Å is substantially shorter than observed with most other nitrogen ligators. A short Ru-N distance has been reported for the ortho-metallated azofluorobenzene chelate[22] (2.020 Å) suggesting that this might be a characteristic feature of azo-containing ligands with ruthenium(II). Together with the short Ru-azo distance in

Table 5. Interplanar angles (deg) between the least squares planes calculated for the pyridine-rings Nj10–Cj15 (pyr(j)), the phenyl groups Cj21–Cj26, phe(j) and the planes defined by Ru – and the azide groups (Ru–NjO–Nj1–Nj2), az(j).

	pyr(1)	pyr(2)	phe(1)	phe(2)	az(1)
Ru1					
py(2)	71				
phe(1)	73	34			
phe(2)	50	43	71		
az(1)	31	78	61	76	
az(2)	77	36	5	75	65

	pyr(3)	pyr(4)	phe(3)	phe(4)	az(3)
Ru2					
pyr(4)	68				
phe(3)	39	51			
phe(4)	54	40	68		
az(3)	19	83	41	73	
az(4)	78	33	43	72	85

$[Ru(azpy)_2(N_3)_2]$ there is also observed a lengthening of the azo N=N to an average value of 1.292 Å. A similar azo-lengthening is observed in ortho-ruthenated azofluorobenzene[22] to 1.31 Å. These azo bond lengths can be compared with that in *trans*-azobenzene (1.24 Å).[23]

A recent report on the structure of an arylazo oxime ruthenium(II) complex shows similar structural features.[24] Here the Ru–N(azo) distance of 1.979(7) Å again shows evidence of considerable multiple bond character, accompanied by a lengthening of the azo N–N distance to 1.292(9) Å.

Our observed ruthenium-azido distances average 2.114 Å, indicative of only a sigma interaction. This distance compares with that observed in $[Ru(N_3)(N_2)(ethylenediamine)_2]^+$ (2.121 Å).[25] The Ru–N distances observed for the four Ru–N_3 groups of the two conformers (from 2.093 to 2.146 Å) appear to exhibit small but significant variations. These

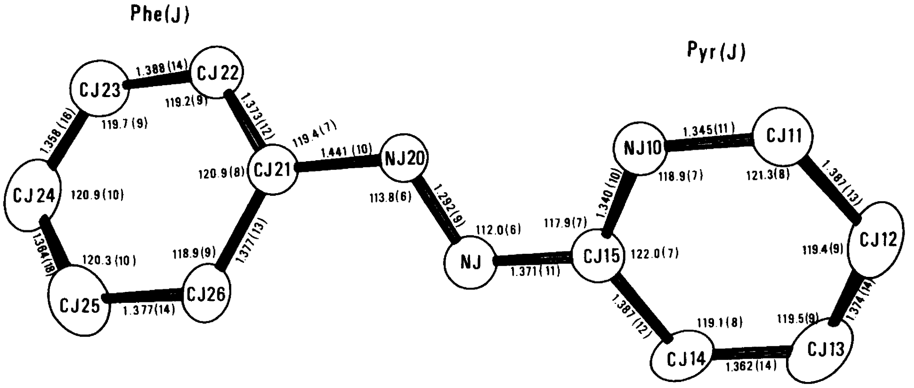


Fig. 3. Molecular structure of coordinated 2-(phenylazo)pyridine (azpy). The bond lengths and bond angles shown are averaged over the four independent azpy ligands. The e.s.d.'s given are the averaged values.

Table 6. Selected Bond Distances (Å).

		Ru–N	N–N	Ref.
Ru bpy$_3$(PF$_6$)$_2$		2.056		16
[bpy$_2$Ru(NO$_2$)]$_2$O		2.078, 2.100		17
		2.071, 2.064		
	bpy	2.094, 2.074		
		2.073, 2.061		
	NO$_2$	2.067, 2.034		
Ru(pyridine)$_6$(BF$_4$)$_2$		2.12		26
Ru(NH$_3$)$_6$I$_2$		2.144		19
Ru(NH$_3$)$_6$(BF$_4$)$_3$		2.104		19
[Ru(NH$_3$)$_5$pyrazine](BF$_4$)$_2$		2.166(NH$_3$); 2.006 (pyrazine)		18
[Ru(NH$_3$)$_5$pyrazine](CF$_3$SO$_3$)$_3$		2.125(NH$_3$); 2.076 (pyrazine)		18
[Ru(ethylenediamine)$_3$][ZnCl$_4$]		2.143, 2.145		20
		2.137, 2.134		
		2.110, 2.119		
trans C$_6$H$_5$N=NC$_6$H$_5$			1.24	22
Ru C$_6$F$_4$N=NC$_6$F$_5$(Ph$_2$P C$_6$H$_4$–C$_5$H$_4$)		2.020	1.310	21

numbers correlate with the Ru-azo distances *trans* to each azido-group, the longest Ru-azo bond occurring *trans* to the shortest Ru–N$_3$. The internal N$_3^-$ distances show no correlation.

We feel that packing may affect the Ru–N$_3$ distances and the *small* differences should not imply any π-interaction. But the shorter azido-distances then cause a repulsion of the *trans* azo-groups through a σ-effect, giving the observed correlation.

Using infrared evidence we had earlier concluded there to be a substantial Ru-azpy π-interaction with concomitant lowering of the azpy azo-bond order in [Ru(azpy)$_2$(N$_3$)$_2$].[4] We were thus able to correlate coligand π-acceptor properties with the observed azo-infrared mode. The structural details discussed above are in complete agreement with this model, lending confidence to our previous arguments.

In our early work with [Ru(azpy)$_2$Cl$_2$] we found evidence for only two *cis*-dichloro isomers, the α- and β-forms.[3] A question remained as to whether α-[Ru(azpy)$_2$Cl$_2$] had *trans*-pyridine or *trans*-azo groups. In the present structure of α-[Ru(azpy)$_2$(N$_3$)$_2$] the former configuration is observed. The missing *cis*-isomer (*trans*-azo-groups) probably has no existence. In the case where *trans*-azo-groups are present (γ-[Ru(azpy)$_2$Cl$_2$], having *trans*-chloride, azo- and pyridine groups) the complex has very low solubility under synthesis conditions and is thus isolated. It does readily isomerize.[3]

Conclusions. [Ru(azpy)$_2$(N$_3$)$_2$] is shown to be a reactive complex displaying stereoretentive reactions under mild conditions. The azpy ligators have been established as pyridine nitrogen and azo-nitrogen adjacent to the phenyl ring; short Ru-azpy bond distances are consistent with the proposal of pronounced metal-ligand π-bonding. In the present structure the *cis*-α-configuration is shown to contain *trans*-pyridines and *cis*-azo-ligators.

A rare example of molecular conformers of a coordination compound has been found.

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