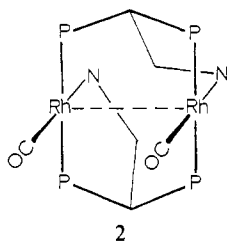


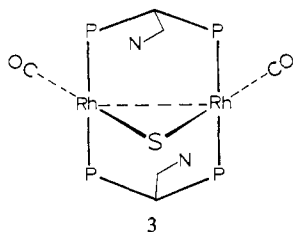
Since this is the first structure determination for a PNP complex, it is not possible to compare these distances with those of other tridentate PNP compounds. It is likely that ring strain is the cause of these long Rh-ligand distances. Indeed, it has been predicted that PNP-type ligands cannot achieve tridentate coordination to a single metal center.¹⁹ The internal angles within the Rh-PNP chelate rings are all small compared with their expected unstrained values. Thus, the Rh-N-C2, N-C2-C1, and C2-C1-P angles are 115.5 (3), 111.8 (5), and 102.7 (3)°, respectively. The Rh-P-C1 angle (84.7 (1)°) is also significantly decreased relative to a normal Rh-dppm value [93.5 (2)° found in [Rh(dppm)₂CO]BF₄²⁶] while the P-C1-P' angle (98.1 (3)°) is increased compared with a normal Rh-dppm value (94.3 (3)°).²⁶ These differences result from the increased folding in the four-membered RhP₂C-dppm type chelate ring about the P-P' vector in the direction of the pyridyl group. This ring folding is obviously caused by the coordination of the pyridyl group. The dihedral angle between the P-Rh-P' and the P-C1-P' planes is 49° and is well outside of the range observed in dppm complexes (0-29.8°).²⁶ The distances between rhodium and the double-bond centers of nbd are 2.04 and 2.05 Å and are within the range 2.00-2.14 Å found in heavy-metal diolefin complexes.^{30,31} The distances and angles within the nbd ligand are normal.

The chelate "bite" angles for the PNP ligand are smaller than those generally observed for four- to five-membered chelate rings. The values for the P-Rh-P' and P-Rh-N angles are 71.25 (6) and 75.9 (1)°, respectively. The N atom is approximately trans to the midpoint of the C10-C10' double bond (N-Rh-midpoint = 168°) while the P atoms are approximately trans to C9 and C9' (P-Rh-C9' = 162°).

Reactivity of [Rh(nbd)(PNP)]BF₄. Complex **1** readily reacts in acetone solution at 25 °C with 1 atm of CO, giving a purple binuclear compound of formula [Rh(PNP)(CO)]₂(BF₄)₂ (**2**). The formulation of this complex is based on IR [$\nu(\text{CO})$ 2002 cm⁻¹, $\nu(\text{py CN})$ 1602 cm⁻¹], ³¹P{¹H} NMR [δ_1 (d of d of d, intensity 1) 62.0, $J_{\text{P-P(trans)}}$ = 293.5 Hz, $J_{\text{Rh-P}}$ = 117.9 Hz, $J_{\text{P-P}}$ = 54.1 Hz; δ_2 (d of d of d, intensity 1) 40.2, $J_{\text{P-P(trans)}}$ = 293.0 Hz, $J_{\text{Rh-P}}$ = 134.3 Hz, $J_{\text{P-P}}$ = 54.0 Hz], and a single-crystal X-ray diffraction analysis.³² The structure of this complex is illustrated in **2** and is consistent with the above spectroscopic



data. This face-to-face dimer has a Rh...Rh separation of 3.054 (1) Å.³² This complex is novel in that it is the first example of a face-to-face dimer with two tridentate bridging ligands. Reaction of **2** with sulfide ion in methanol solution gives an orange-red complex **3** which is formulated as Rh₂-



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(32) The details of this X-ray analysis will be published elsewhere.

(μ -S)(CO)₂(PNP)₂. The proposed structure of **3** is that of a sulfide-bridged A-frame where the N atoms of the PNP ligands are unbound. This structure is based on Ir [$\nu(\text{py CN})$ 1582 cm⁻¹, $\nu(\text{CO})$ 1935 cm⁻¹] and ³¹P{¹H} NMR [δ (CDCl₃ solution) 30.7 (PNP, symmetric multiplet with two principal lines separated by ~139 Hz)]. The $\nu(\text{py CN})$ stretching frequency is very similar to that of the free PNP ligand, and the ³¹P NMR spectrum is typical of dppm-bridged A-frames of rhodium.³³ Crystals suitable for a single-crystal X-ray analysis have not yet been obtained for **3**.

Although the study of the reactivity and catalytic properties of these novel PNP complexes is in its preliminary stages, the above results illustrate a rich chemistry. Complex **1** also reacts with 1 atm of H₂, giving what appears to be a tetrahydrido binuclear complex. Preliminary results also show that **1** is an excellent aldehyde decarbonylation catalyst. The details of these studies will be presented in a future publication.

Acknowledgment. Support of this research through a grant from the National Science Foundation is gratefully acknowledged (NSF No. CHE 81-08490). We also thank the NSF for partial support for our X-ray diffraction and structure-solving equipment (NSF Grant No. CHE 77-28505). The Johnson-Matthey Co. is gratefully acknowledged for a generous loan of RhCl₃·H₂O. M.P.A. is a participant in the U.S. Air Force Institute of Technology Graduate School Program. B.M.M. acknowledges the Graduate School of Creighton University for a Summer Faculty Research Fellowship.

Registry No. **1**, 86436-86-4; **2**, 86455-87-0; **3**, 86436-87-5; [(nbd)RhCl]₂, 12257-42-0; PNP, 60398-55-2; chlorodiphenylphosphine, 1079-66-9; 2-picoline, 109-06-8.

Supplementary Material Available: ORTEP stereoview of [Rh(nbd)(PNP)]⁺ and tables of general temperature factor expressions, calculated hydrogen atom positional parameters, and calculated and observed structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Bis(bipyrazine)ruthenium(II) Complexes: Characterization, Spectroscopy, and Electrochemistry

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Recently we have reported the synthesis of an important new photocatalyst, the ruthenium(II) tris(bipyrazine) cation.¹ The chemical, physical, and photophysical properties of this cation have been discussed.^{2,3} Moreover, it has been shown to form a series of protonated species in acid media, including a hexaprotonated species in concentrated sulfuric acid.⁴

We believe that (bipyrazine)ruthenium(II) complexes may have an important role to play in the development of future photocatalysts and, to this end, report the synthesis and characterizations of bis(bipyrazine)ruthenium(II) complexes, *cis*-Ru(bpz)₂X₂ where X is Cl⁻, Br⁻, I⁻, SCN⁻, NO₂⁻, H₂O, OH⁻, CO₃²⁻, and oxalate. The complexes are characterized

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Table I. ^1H NMR Spectra of $\text{Ru}(\text{bpz})_2\text{X}_2$ Species^a

complex	H_3	H_5	H_6	H_3'	H_5'	H_6'	$J_{3,6}$	$J_{3',6'}$	$J_{5,6}$	$J_{5',6'}$
$\text{Ru}(\text{bpz})_2(\text{NO}_2)_2$	10.02	9.03	9.63	9.93	8.44	7.88	1.0	1.0	3.2	3.2
$\text{Ru}(\text{bpz})_2(\text{NCS})_2$	10.02	9.08	9.23	9.85	8.38	7.89	0.9	0.9	3.2	3.4
$\text{Ru}(\text{bpz})_2\text{Cl}_2$	10.03	8.98	9.92	9.86	8.28	7.88	0.8	0.8	3.3	3.3
$\text{Ru}(\text{bpz})_2\text{Br}_2$	10.03	9.00	10.11	9.86	8.32	7.92	0.9	0.9	3.5	3.3
$\text{Ru}(\text{bpz})_2\text{I}_2$	10.00	8.99	10.33	9.84	8.33	7.92	0.9	0.9	3.3	3.3

^a Recorded in $\text{Me}_2\text{SO}-d_6$. From tetramethylsilane in ppm; J in Hz. H_3' , H_5' , and H_6' are in the ring trans to coordinated ligands other than bipyrazine.

by electronic, vibrational, and NMR spectra and electrochemistry.

Experimental Section

Electronic spectra were recorded with a Perkin-Elmer Hitachi Model 340 microprocessor UV/vis spectrometer; infrared spectra were recorded with a Beckman IR12 spectrometer; ^1H NMR spectra were obtained with a Varian EN360 60-MHz NMR spectrometer. Tetramethylsilane at 0.00 ppm or residual protons of dimethyl- d_6 sulfoxide at 2.50 ppm were used as internal references. Conductivity data were obtained with a Wayne-Kerr conductivity bridge, and electrochemical data, with use of Princeton Applied Research equipment⁵ (and cell setup²) as previously described.

Preparation of Complexes. $\text{Ru}(\text{bpz})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. This complex was initially reported via the photoanation of $\text{Ru}(\text{bpz})_3\text{Cl}_2$. It may be prepared directly, as follows.

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (0.35 g) and bpz (0.6 g) were stirred and refluxed in DMF (50 mL). After 11 h, the purple solution was filtered and ether added to precipitate $\text{Ru}(\text{bpz})_2\text{Cl}_2$. The crude product was washed with ether and recrystallized from acetonitrile to yield black microcrystals of $\text{Ru}(\text{bpz})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (yield 0.6 g, 85%). Anal. C, H, N, Cl.

The bromo and iodo complexes were prepared in a fashion similar to the in situ generation of the corresponding ruthenium halides, as follows.

Preparation of in Situ RuX_3 ($\text{X} = \text{Br}, \text{I}$). To a solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (1.5 g) in water (40 mL) was added 10 N NaOH (2 mL). The solution was boiled and filtered, and the black precipitate of $\text{RuO}_{2+x} \cdot y\text{H}_2\text{O}$ was washed with water and acetone. After drying, the oxide was placed in a beaker together with concentrated HX (30 mL; $\text{X} = \text{Br}$ or I). The mixture was digested at low temperature until it evaporated almost to dryness (overheating can lead to the formation of insoluble products). The ruthenium halide was then vacuum dried. The yield was almost quantitative. The iodide should be used fresh since it becomes inert over a period of time.

$\text{Ru}(\text{bpz})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was prepared as for the chloride. Anal. C, H, N, Br.

$\text{Ru}(\text{bpz})_2\text{I}_2$ was prepared in an analogous fashion except that the product was thrown out of solution by adding methanol (75 mL) and ether (300 mL) and storing the solution in a freezer overnight. Anal. C, H, N, I.

$\text{Ru}(\text{bpz})_2(\text{NO}_2)_2 \cdot 0.5\text{H}_2\text{O} \cdot 0.5\text{CH}_3\text{CN}$. $\text{Ru}(\text{bpz})_2\text{Cl}_2$ (0.5 g) and sodium nitrite (1.0 g) were refluxed in 1:1 ethanol/water (30 mL) for 1 h with constant stirring. When the mixture was cooled and left overnight in the freezer, the orange red nitro product (0.35 g, 66%) was obtained. Anal. C, H, N.

$\text{Ru}(\text{bpz})_2(\text{NCS})_2 \cdot 1.5\text{H}_2\text{O}$. This was prepared in the same fashion as the nitro derivative, but with use of ammonium thiocyanate (2.0 g). However, after 1.5 h, additional water (10 mL) was added and the ethanol removed by azeotropic distillation. After storage overnight at room temperature, black microcrystals of the thiocyanate product (0.4 g, 70%) were obtained. Anal. C, H, N.

$\text{Ru}(\text{bpz})_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$. $\text{Ru}(\text{bpz})_2\text{Cl}_2$ (1.0 g) and ammonium oxalate (2.0 g) were placed in a 4:1 water/ethanol solution (50 mL) and refluxed for 2 h with constant stirring. The red solution was filtered hot and the filtrate cooled to room temperature. The black microcrystals that formed were washed with water and ethanol (yield 0.6 g, 58%). Anal. C, H, N.

$\text{Ru}(\text{bpz})_2(\text{CO}_3) \cdot 5\text{H}_2\text{O}$. $\text{Ru}(\text{bpz})_2\text{Cl}_2$ (0.5 g) and potassium carbonate (1.0 g) were placed in 1:1 ethanol/water solution (30 mL) and refluxed for 2 h with constant stirring. The hot solution was

filtered and placed in a freezer overnight. Black microcrystals of the carbonate species were collected and washed with water and ethanol (yield 0.4 g, 74%). Anal. C, H, N. (The H analysis was slightly high.) Both the oxalate and carbonate are only very sparingly soluble in organic solvents, limiting the collection of data on these complexes. The complexes are soluble in water, and the low conductivity of such solutions infers that little hydrolysis takes place at least at room temperature.⁶

Results and Discussion

The complexes $\text{Ru}(\text{bpz})_2\text{X}_2$, $\text{X} = \text{Cl}^-$, Br^- , I^- , SCN^- , and NO_2^- , are nonconducting in acetonitrile, consistent with a six-coordinate un-ionized pseudooctahedral formulation.

The ^1H NMR spectra are fully consistent with a cis stereochemistry, the trans form probably being inhibited because of proton-proton repulsion between trans planar bpz groups. The ^1H NMR spectrum of $\text{Ru}(\text{bpz})_2\text{Cl}_2$ has already been adequately discussed.² Chemical shifts for the various protons are reported in Table I, with assignments based upon our earlier analysis.² Briefly, the complexes have C_2 symmetry, and thus each complex contains two magnetically inequivalent pyrazine moieties. The protons of one pyrazine ring are influenced by the anisotropic effect of a neighboring pyrazine ring and experience chemical shifts similar to those of the tris(bipyrazine) cation.² Protons of the other pyrazine moiety will be shifted downfield relative to the other ring as confirmed nicely by experiment (Figure 3 of ref 2; Table I). As shown in Table I, the protons H_3 , H_3' , H_5 , H_5' , and H_6' remain fairly constant whereas the chemical shift of H_6 varies considerably with variation of X. For $\text{X} = \text{Cl}^-$, Br^- , and I^- , H_6 shifts downfield as the radius of X increases, suggesting a van der Waals deshielding interaction. For $\text{X} = \text{NO}_2^-$ and SCN^- , the magnetic anisotropy of X must also be taken into account. The J values given in Table I are slightly dependent on the ligand. The exact nature of this dependence requires further study.

The IR spectrum of the nitro complex shows N-O stretching vibrations at 1300 and 1350 cm^{-1} consistent with N-bound nitro coordination, rather than O-bound nitrito.⁷ The thiocyanate derivative shows $\nu(\text{CN})$ at 2100 cm^{-1} (broad), but the $\nu(\text{CS})$ frequency is apparently obscured by bpz absorption. In parallel with $\text{Ru}(\text{bpy})_2(\text{NCS})_2$,⁸ it is probable that the thiocyanate is N bound.⁹ Indeed, the data to be discussed below would be inconsistent with S bonding.

Infrared spectra for the carbonate and oxalate species are consistent with a coordinated anion in the solid state. The carbonate complex exhibits bands at ca. 1600, 1260, 1040, 840, and 760 cm^{-1} , consistent with bidentate bound carbonate.¹⁰ The oxalate complex exhibits a broad band at 1690 cm^{-1} , plus other absorption, consistent with bound rather than ionic oxalate.¹⁰

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Table II. Electrochemical Data in Acetonitrile (V vs. SCE)^a

complex	Ru(III)/ Ru(II)	bpz/bpz ⁻	bpz ⁻ /2bpz ⁻
Ru(bpz) ₃ ²⁺ ^b	1.86	-0.80	-0.98, -1.24
Ru(bpz) ₂ (NO ₂) ₂	1.18 ^c		
Ru(bpz) ₂ (NCS) ₂	0.94 ^d	-0.93	-1.18 ^c
Ru(bpz) ₂ Cl ₂	0.80	-1.04 ^c	-1.27 ^c
Ru(bpz) ₂ Br ₂	0.79	-1.09 ^c	-1.22 ^c
Ru(bpz) ₂ I ₂	0.80 ^d	-1.05 ^c	-1.18 ^c

^a 0.1 M tetraethylammonium hexafluorophosphate. All data are averages of anodic and cathodic peaks at 100 mV/s scan rates. The waves are reversible except for those indicated otherwise.

^b Data from ref 2. ^c Partially reversible. ^d Irreversible.

Electrochemical data are reported in Table II. The bpz ligands are reduced at potentials similar to that of the tris(bipyrazine) cation.² The first reduction potential is about 200 mV less positive than for the tris(bipyrazine)ruthenium(II) cation probably because the polarizing power of the ruthenium has been reduced by the replacement of a hard bipyrazine ligand with softer anions. This is reflected by the oxidation couple Ru(III)/Ru(II), which is dependent upon X. With X a halogen, the potentials are less positive than with the harder nitrogen ligands, NO₂⁻ and SCN⁻, and much less than for the tris(bipyrazine) case with X = bpz.

The electronic spectra of these bis(bipyrazine) complexes (Table III) show two MLCT bands, one near 18 000 and the other near 25 000 cm⁻¹, due to transitions from Ru (t_{2g})⁶ to the first two acceptor π* orbitals on the coupled bipyrazine ligands.² The UV absorptions near 32 000 and 42 000 cm⁻¹ are internal π-π* transitions on the bipyrazine ligands. The shoulder between these two transitions may be π-π* or perhaps n-π*. It is not likely to be an MLCT transition, though tentatively assigned as such in ref 2 since, unlike the other MLCT transitions, it is almost invariant in position with change in X.

The MLCT bands shift to the red in passing from the very hard bpz to the hard nitrogen (SCN⁻ and NO₂⁻) and oxygen ligands (carbonate etc.) to the softer halides, the charge-transfer frequencies being directly proportional to the Ru(III)/Ru(II) oxidation potentials. As charge is placed on the ruthenium atom, making it less positive, this facilitates both electrochemical oxidation and charge transfer from metal to ligand.

Table III. Electronic Spectra of Ru(bpz)₂X₂ Species^a

complex	ruthenium to diimine MLCT		π-π* bipyrazine	
	Wavenumber (log ε)	Wavenumber (log ε)	Wavenumber (log ε)	Wavenumber (log ε)
Ru(bpz) ₃ ²⁺	22 575 (4.18)	29 155 (4.27)	33 900 (4.79)	37 455 (4.34)
Ru(bpz) ₂ (NO ₂) ₂	20 660 (3.94)	28 735 (3.97)	41 495 (4.37)	
		37 455 (4.34)	32 365 (4.57)	37 735 sh
Ru(bpz) ₂ (NCS) ₂	19 010 (3.96)	26 740 (3.95)	42 020 (4.29)	
			32 155 (4.59)	37 455 sh
Ru(bpz) ₂ Cl ₂	18 020 (4.03)	25 315 (3.94)	42 200 (4.41)	
			32 050 (4.54)	
Ru(bpz) ₂ Br ₂	18 250 (3.99)	25 510 (3.91)	41 325 (4.31)	
			31 950 (4.53)	38 170 sh
Ru(bpz) ₂ I ₂	18 115 (3.90)	25 510 (3.89)	42 020 (4.36)	
			31 450 (4.46)	
Ru(bpz) ₂ (Ox) ^{b,c}	19 380 (4.08)	26 740 (3.97)	42 735 (4.43)	
			32 360 (4.70)	37 455 sh
Ru(bpz) ₂ CO ₃ ^c	20 080 (3.93)	26 320 sh	41 495 (4.30)	
			32 360 (4.59)	37 595 sh
Ru(bpz) ₂ (H ₂ O) ₂ ^{2+,d}	20 240 (4.11)	27 780 sh	41 840 (4.22)	
			32 680 (4.74)	37 595 sh
Ru(bpz) ₂ (H ₂ O)(OH) ^{+,e}	18 870 (4.04)	26 040 (3.96)	42 195 (4.33)	
			32 260 (4.71)	38 460 sh
Ru(bpz) ₂ (OH) ₂ ^{c,f}	17 480 (4.05)	24 690 (3.97)	42 020 (4.37)	
			31 550 (4.65)	38 460 sh
			42 195 (4.36)	

^a Data in wavenumbers, log ε in parentheses; all data in acetonitrile except where noted. Data for the tris(bipyrazine) complex from ref 2.

^b Oxalate. ^c In water. ^d pH 3. ^e pH ca. 8.5. ^f pH 14.

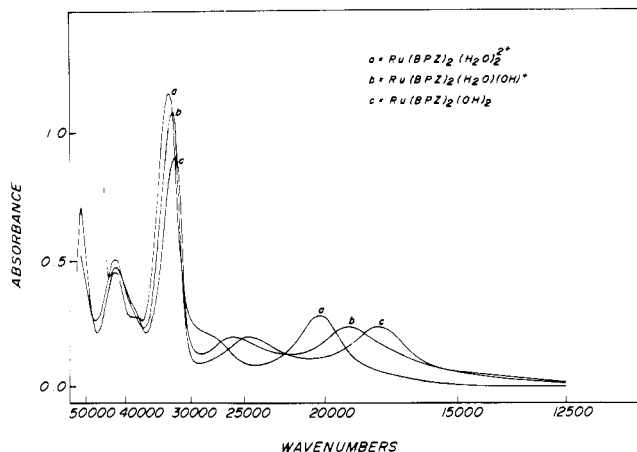


Figure 1. Electronic spectra of (a) Ru(bpz)₂(H₂O)₂²⁺ in water at pH 3, (b) Ru(bpz)₂(H₂O)(OH)⁺ in water at pH 8.5, and (c) Ru(bpz)₂(OH)₂ in water at pH 14.

Aquo and Hydroxy Species. If dilute perchloric acid is added to Ru(bpz)₂CO₃, the cation [Ru(bpz)₂(H₂O)₂]²⁺ is formed. Although it is not isolated, this species has electronic spectra (Table III, Figure 1) consistent with the slightly harder nature of water relative to halogen and consistent with previous data reported for the bipyridine analogue.¹⁰ If NaOH is added to this solution, two new species may be detected (Figure 1). In strong base solution, the two MLCT charge-transfer bands are shifted 2700–3000 cm⁻¹ to the red. When an acid solution of the dihydrate complex is titrated with base (or a basic solution is treated with acid), an intermediate is seen, with spectra lying between these two species, i.e. shifted about 1300–1800 cm⁻¹ to the red of the dihydrate. Indeed, titration of an acid solution with standard NaOH results in two successive sets of isosbestic points being observed; plotting the peak position of the lower energy MLCT band against titer yields a double sigmoidal curve with inflection points at pH 7.6 and pH 9.8.

These data are entirely consistent with the hydrolysis of [Ru(bpz)₂(H₂O)₂]²⁺ with a pK_a of 7.6 to yield [Ru(bpz)₂(H₂O)(OH)]⁺ followed by its hydrolysis with a pK_a of 9.8 to yield Ru(bpz)₂(OH)₂. Corresponding data for the bipyridine analogue do not appear to have been reported. However, the pK_a value for the hydrolysis of Ru(bpy)₂(py)(H₂O)²⁺ is 10.8,¹²

and the consecutive values for the rhodium(III) and rhodium(II) species $\text{Rh}(\text{bpy})_2(\text{H}_2\text{O})_2^{3+}$ and $\text{Rh}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$ are 4.8, 6.87 and 8.6, 11.1, respectively;¹³ these results are consistent with our data.

The MLCT band positions of the hydroxy species span the halide data, suggesting that hydroxide ion acts as a soft ligand toward ruthenium(II), transferring appreciable charge density to the metal.

Further photochemical studies of these species are in hand. We note that the hydroxy species may be useful starting materials toward the generation of Ru(IV) oxo species, which would parallel those formed with bipyridine^{12,14} but would be much stronger oxidizing agents. Indeed, the procedures outlined here provide new synthetic routes into bis(bipyrazine)ruthenium(II) chemistry and later may allow the generation of bis(bipyrazine)osmium(II) complexes whose bipyridine analogues are of especial photocatalytic interest.¹⁵

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Registry No. $\text{Ru}(\text{bpz})_3^{2+}$, 75523-96-5; $\text{Ru}(\text{bpz})_2(\text{NO}_2)_2$, 86497-09-8; $\text{Ru}(\text{bpz})_2(\text{NCS})_2$, 86497-10-1; $\text{Ru}(\text{bpz})_2\text{Cl}_2$, 80907-59-1; $\text{Ru}(\text{bpz})_2\text{Br}_2$, 86497-11-2; $\text{Ru}(\text{bpz})_2\text{I}_2$, 86497-12-3; $\text{Ru}(\text{bpz})_2(\text{Ox})$, 86497-13-4; $\text{Ru}(\text{bpz})_2\text{CO}_3$, 86497-14-5; $\text{Ru}(\text{bpz})_2(\text{H}_2\text{O})_2^{2+}$, 86497-15-6; $\text{Ru}(\text{bpz})_2(\text{H}_2\text{O})(\text{OH})^+$, 86497-16-7; $\text{Ru}(\text{bpz})_2(\text{OH})_2$, 86497-17-8; bpz, 10199-00-5.

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Nitrogen-15 NMR Spectroscopy of Bis(aspartato)cobaltate(III)

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The nuclear magnetic resonance spectroscopy of nitrogen in coordination compounds is an area of considerable potential interest. Nitrogen is a constituent of many ligands that are important in coordination chemistry and biochemistry. Several researchers have tried to elucidate the main factor that governs the nitrogen-15 chemical shift of coordination complexes, but this main factor has not yet been discovered.¹⁻⁴ It is necessary to collect a great deal of ¹⁵N chemical shift information concerning metal complexes. We have given a method for assigning proton magnetic resonance spectra of diamagnetic

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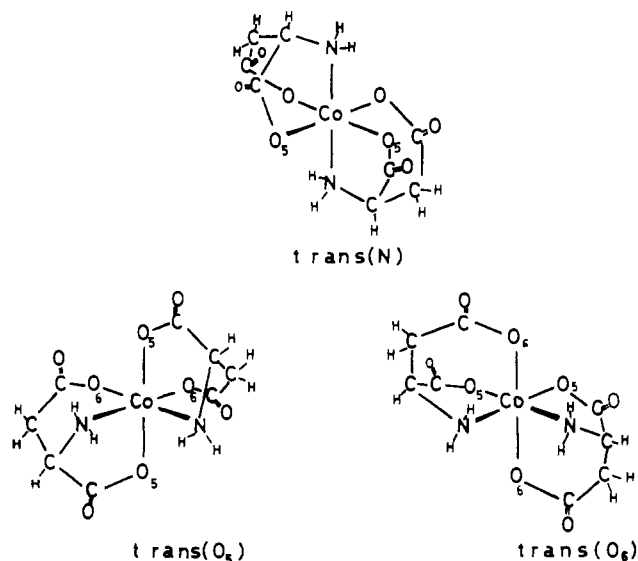


Figure 1. The three isomers of $[\text{Co}(\text{L-asp})_2]^-$.

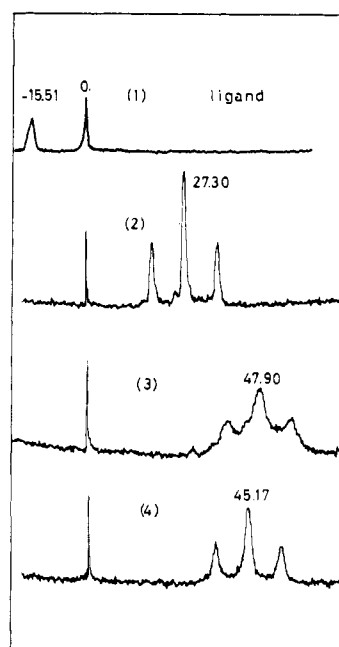


Figure 2. ¹⁵N NMR spectra in H_2O : (1) free ligand at pH 9.0; (2) *trans*(N) isomer; (3) *trans*(O₅) isomer; (4) *trans*(O₆) isomer.

cobalt complexes and found a general trend for the chemical shifts of a proton in a H-C-N-Co-X fragment, where X is a nitrogen or an oxygen atom and occupies the *trans* (to N) position.⁵ The proton resonates at higher or lower field according to whether X is oxygen or nitrogen. Freeman et al.⁶⁻⁸ at first elucidated qualitatively and Yoneda et al.^{9,10} studied quantitatively that these shifts were primarily determined by the magnetic anisotropy of the central cobalt ion. It would

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