10 M^{-1} even though the pK_a for 3-BzA is ~ 6[22] and the pK_a for CNpy is ~ 2.[22] This decrease from the value expected on the basis of pK_a considerations suggests destabilization by the 6-amino group. It is clear from these and unpublished data[23] that stability constants for 4-cyanopyridine cobaloximes are higher when X has a lower trans influence. However, for the adenine derivatives, there must be a point where this trend begins to reverse, since as the Co–N(7) bond length decreases (as the trans influence of X decreases) repulsive interactions between the amino group and the dimethylglyoxime equatorial plane must increase. The dissymmetry in bond angles about N(7), alluded to above, would become even more marked, and very poor overlap between the N(7) lone pair and the appropriate metal-bonding orbitals would result.[1] We were not, in fact, successful in preparing any N(7)-bound 6-aminopurine–cobaloxime complexes with weak trans-directing ligands, although a number of preparative approaches were employed.

Furthermore, the exocyclic amino group at C(6) of the adenine derivatives is not able to form as strong a hydrogen bond to the equatorial cobaloxime frame as it can in the acac complex. The oxygen atoms of the cobaloxime complex are already involved with hydrogen bonding between themselves. A weak hydrogen bond is observed (Table IV), but its contribution to the overall molecular stability is expected to be less than that of the bifurcated system in the acac complex.[3] The consequences of interligand interactions in adenine complexes are thus, once again, underscored by a comparison of the general properties of the cobaloxime and acac complexes of 3-substituted adenine derivatives.

Acknowledgment. This investigation was supported by the National Institutes of Health through Public Health Services Grants GM 20544 and GM 29222.

Registry No. $[(3\text{-BzA})Co(DH)_2(P(O)(OCH_3)_2)]\cdot H_2O\cdot EtOH$, 76550-08-8; $(3\text{-BzA})Co(DH)_2(CH_2Br)$, 76550-09-9; $(3\text{-BzA})Co(DH)_2(CH_3)$, 76550-10-2; $(3\text{-BzA})Co(DH)_2(i\text{-}C_3H_7)$, 76550-11-3; $(3\text{-BzA})Co(DH)_2(C_2H_5)$, 76550-12-4; $(3\text{-ECMA})Co(DH)_2(P(O)(OCH_3)_2)$, 76550-13-5; $(3\text{-ECMA})Co(DH)_2(CH_2Br)$, 76550-14-6; $(3\text{-ECMA})Co(DH)_2(CH_3)$, 76550-15-7; $(3\text{-ECMA})Co(DH)_2(i\text{-}C_3H_7)$, 76550-16-8; $(3\text{-MeA})Co(DH)_2(P(O)(OCH_3)_2)$, 76550-17-9; $(3\text{-MeA})Co(DH)_2(CH_3)$, 76550-18-0; $(9\text{-MeA})Co(DH)_2(P(O)(OCH_3)_2)$, 76550-19-1; $(9\text{-MeA})Co(DH)_2(CH_3)$, 76550-20-4; $(9\text{-MeA})Co(DH)_2(i\text{-}C_3H_7)$, 76550-21-5; $(H_2O)Co(DH)_2(P(O)(OCH_3)_2)$, 56403-87-3; $(H_2O)Co(DH)_2(i\text{-}C_3H_7)$, 28132-41-4; $(H_2O)Co(DH)_2(C_2H_5)$, 26025-30-9; $(H_2O)Co(DH)_2(CH_3)$, 25360-55-8; $(H_2O)Co(DH)_2(CH_2Br)$, 76550-22-6; $(Me_2SO)Co(DH)_2(CH_3)$, 25482-32-0; $(Me_2SO)Co(DH)_2(P(O)(OCH_3)_2)$, 76550-23-7; $(Me_2SO)Co(DH)_2(i\text{-}C_3H_7)$, 64687-69-0; $(Me_2SO)Co(DH)_2(CH_2Br)$, 76550-24-8; $(Me_2SO)Co(DH)_2(C_2H_5)$, 76550-25-9.

Supplementary Material Available: Tables of elemental analyses, ^1H NMR data, nonhydrogen atom thermal parameters, hydrogen atom parameters, and observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Arkansas, Fayetteville, Arkansas 72701

Crystal and Molecular Structure of $(C_2H_4)(Cl)Pt(\mu\text{-}Cl)(\mu\text{-}C_3H_3N_2)Pt(Cl)(C_2H_4)$, a Binuclear Platinum(II) Complex with a Single Pyrazolide Bridge

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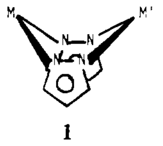
The binuclear diplatinum(II) complex $(C_2H_4)(Cl)Pt(\mu\text{-}Cl)(\mu\text{-}C_3H_3N_2)Pt(Cl)(C_2H_4)$ crystallizes in space group $P2_1/n$ (centrosymmetric, $Z = 4$) with $a = 8.099$ (1) Å, $b = 17.189$ (2) Å, $c = 9.895$ (1) Å, and $\beta = 116.86$ (1)°. The structure was solved by standard Patterson–Fourier methods to $R = 0.040$ for 1182 observed reflections. The Pt_2ClN_2 ring is planar within 0.09 (1) Å, and the plane of the pyrazolide ring makes a 5.7 (4)° angle with this plane. The entire complex, exclusive of the olefin molecules, is planar within 0.35 (2) Å.

Introduction

Binuclear complexes are of interest for their potential as homogeneous catalysts,[1] as models for the transition state in inner-sphere electron transfer,[2] as models for metalloprotein redox centers,[3] and for the unusual electronic and magnetic properties which arise for cases involving strong metal–metal interaction.[4] The properties (chemical and structural) of these materials are strongly dependent upon the mode of linkage (bridging ligand vs. metal–metal bonds) between the metal centers. The pyrazolide anion ($C_3H_3N_2^-$, abbreviated pz) produced by removal of the N-1 proton of pyrazole ($C_3H_4N_2$) is a versatile bridging ligand found in a number of binuclear complexes and higher metallooligomers.[5-7] For the majority of cases, the intermetallic bridges involve two or more pyrazolide or pyrazolyl groups (**1**, **2**). None of the previously observed cases of pyrazolide-bridged binuclear species involving



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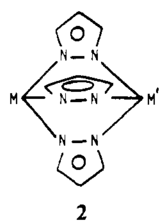

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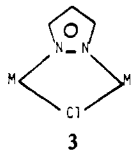

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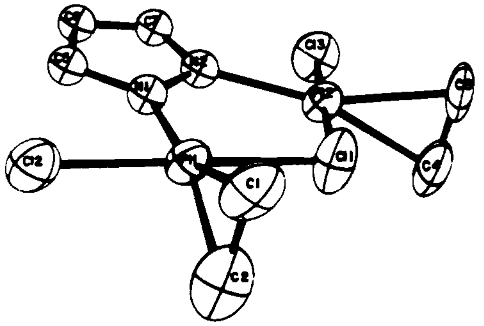

Figure 1. ORTEP diagram of $(C_2H_4)(Cl)Pt(\mu\text{-}Cl)(\mu\text{-}pz)Pt(Cl)(C_2H_4)$.

a single pz group has been characterized structurally. We wish to report the X-ray crystal structure of $(Cl)(C_2H_4)Pt(\mu\text{-}C_3H_3N_2)(\mu\text{-}Cl)Pt(C_2H_4)(Cl)$.

Binuclear species involving bis(pyrazolide) bridges (**1**) usually exhibit a boat conformation for the $M(NN)_2M'$ six-membered central ring; however, for the title complex the central five-membered ring (Pt_2N_2Cl, **3**) is relatively planar. The planarity of this portion of the structure and other observations noted below suggest a π-bonding interaction between the ring and the platinum(II) centers.

Experimental Section

All the materials used were reagent grade chemicals and were used without further purification. The preparation of the title complex has been reported previously.[8] Bright yellow needle-shaped crystals of $(Cl)(C_2H_4)Pt(\mu\text{-}pz)(\mu\text{-}Cl)Pt(C_2H_4)(Cl)$ were obtained by the slow evaporation of a chloroform solution. A single crystal with dimensions 0.038 × 0.031 × 0.198 mm was mounted with epoxy on a glass fiber. Weissenberg photographs indicated the monoclinic space group $P2_1/n$ (centrosymmetric, $Z = 4$). The unit cell parameters were obtained by a least-squares treatment of 23 reflections ($99° \geq 2\theta \geq 58°$). The unit cell dimensions (Cu $K\alpha_1$, $\lambda = 1.5405$ Å) are $a = 8.099$ (1) Å, $b = 17.189$ (2) Å, $c = 9.895$ (1) Å, and $\beta = 116.86$ (1)°. The calculated density of the crystal is 3.35 g/cm^3.

Intensity data were collected by the θ–2θ scan technique on a GE XRD-5 manual diffractometer using Zr-filtered Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation. A scan of 2° at a rate of 2° min^{-1} was used. The intensities of 1646 independent reflections ($2\theta \leq 45°$) were measured, and of these 1203 were considered observed ($I > 3\sigma$). An additional 21 reflections were excluded from the refinement due to human error in the manual recording of the data. During the data collection, two standard reflections were examined regularly to detect crystal degradation (the total intensity decrease was 12%). The raw intensities were scaled by a linear average of the standard reflection intensities at the start and end of a given data collection period. The μ(Mo $K\alpha$) value was 245.42 cm^{-1}. An absorption correction was made, with use of summation points every 0.018 mm; the correction factors (for I) varied from 0.34 to 0.55.

The positions of the platinum atoms were determined by Patterson methods and the remaining nonhydrogen atoms located with use of subsequent Fourier maps. The atom positions were refined by full-matrix least-squares methods where $wt = 1/(2F_{min} + F_o + 2F_o^2/F_{max})$. The temperature factors of the pyrazolide group atoms were refined isotropically and all other nonhydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms could not be located on a difference Fourier map; therefore, hydrogen atoms for the pz ring were added for the final refinement and restricted to calculated positions (C–H = 0.95 Å). The structure refined to $R = 0.040$ and $R_w = 0.057$. A final difference Fourier map showed 18 peaks with intensities ranging from 0.7 to 1.7 e/Å^3, all located within 1.25 Å of a platinum atom position. The final $\Delta F/\sigma$ values did not show a dependence on F or θ. In the final cycle of refinement no parameter shifted by more than 0.19σ.

Table I. Final Positional and Thermal Parameters with Esd's in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Pt(1)	0.2752 (1)	0.40950 (4)	0.44674 (8)	3.56
Pt(2)	0.2624 (1)	0.59162 (4)	0.64432 (8)	3.64
Cl(1)	0.3081 (9)	0.4595 (3)	0.6726 (5)	5.70
Cl(2)	0.2414 (7)	0.3535 (3)	0.2277 (5)	4.84
Cl(3)	0.2291 (8)	0.7235 (3)	0.6256 (6)	5.70
C(1)	0.438 (4)	0.310 (1)	0.562 (2)	5.66
C(2)	0.251 (3)	0.295 (1)	0.531 (2)	5.16
C(3)	0.429 (4)	0.605 (1)	0.887 (2)	5.79
C(4)	0.242 (4)	0.592 (1)	0.858 (2)	6.28
C(5)	0.146 (3)	0.533 (1)	0.201 (2)	4.3 (4)
C(6)	0.090 (3)	0.610 (1)	0.180 (2)	4.9 (4)
C(7)	0.113 (2)	0.636 (1)	0.312 (2)	3.7 (4)
N(1)	0.199 (2)	0.515 (1)	0.347 (1)	2.6 (2)
N(2)	0.183 (2)	0.584 (1)	0.417 (2)	3.2 (3)
H(C5)	0.144	0.497	0.124	5.0
H(C6)	0.042	0.637	0.087	5.0
H(C7)	0.085	0.690	0.325	5.0

[a] Equivalent isotropic temperature factors B_{eq} (Å^2) have been calculated from $B_{eq} = 4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$. For isotropic atoms the normal temperature factor B is listed.

Table II. Selected Interatomic Distances (Å) and Angles (Deg) with Esd's in Parentheses

atoms	dist	atoms	angle
Pt(1)–Pt(2)	3.717 (1)	Pt(1)–Cl(1)–Pt(2)	108.1 (2)
Pt(1)–Cl(2)	2.272 (6)	Cl(1)–Pt(1)–N(1)	90.9 (4)
Pt(2)–Cl(3)	2.280 (6)	Cl(1)–Pt(2)–N(2)	90.3 (5)
Pt(1)–Cl(1)	2.294 (6)	Cl(2)–Pt(1)–N(1)	92.1 (4)
Pt(2)–Cl(1)	2.299 (6)	Cl(3)–Pt(2)–N(2)	90.3 (5)
Pt(1)–N(1)	2.03 (1)	Pt(1)–N(1)–N(2)	126 (1)
Pt(2)–N(2)	2.05 (2)	Pt(2)–N(2)–N(1)	122 (1)
Pt(1)–C(1)	2.15 (2)	Cl(2)–Pt(1)–X(1)[a]	87.9 (7)
Pt(1)–C(2)	2.18 (2)	Cl(3)–Pt(2)–X(2)[a]	89.7 (7)
Pt(2)–C(3)	2.17 (2)	Cl(1)–Pt(1)–X(1)[a]	89.1 (7)
Pt(2)–C(4)	2.19 (3)	Cl(1)–Pt(2)–X(2)[a]	88.5 (7)
Pt(1)–X(1)[a]	2.04 (2)	Cl(1)–Pt(1)–Cl(2)	176.9 (2)
Pt(2)–X(2)[a]	2.06 (2)	Cl(1)–Pt(2)–Cl(3)	177.5 (2)
N(1)–N(2)	1.41 (2)	N(1)–Pt(1)–X(1)[a]	178.4 (8)
N(1)–C(5)	1.35 (3)	N(2)–Pt(2)–X(2)[a]	178.5 (8)
N(2)–C(7)	1.29 (2)	N(1)–N(2)–C(7)	107 (1)
C(5)–C(6)	1.37 (3)	N(2)–N(1)–C(5)	106 (1)
C(6)–C(7)	1.31 (3)	N(1)–C(5)–C(6)	108 (2)
C(1)–C(2)	1.43 (4)	N(2)–C(5)–C(6)	112 (2)
C(3)–C(4)	1.43 (4)	C(5)–C(6)–C(7)	107 (2)

[a] X(1) = midpoint between C(1) and C(2); X(2) = midpoint between C(3) and C(4).

Final atom positional parameters are collected in Table I. Selected bond distances and bond angles are summarized in Table II. Table III contains selected best-planes information, and the dihedral angles are listed in Table IV. Figure 1 is an ORTEP plot of a single molecule, and Figure 2 shows a stereoview packing diagram. Table V (supplementary material) gives the thermal parameters for the nonhydrogen atoms.

Results and Discussion

The overall planarity of the binuclear complex was not anticipated. The majority of binuclear species involving two pyrazolide bridges exhibit a boat conformation for the central six-membered ring ($M(NN)_2M'$; see **1**). A similar puckered Pt_2N_2Cl central ring also might be expected for the title complex. Puckering of the central ring would help relieve a close contact between the protons of the pyrazolide group and the adjacent nonbridging chloride ligands (H(C5)–Cl(2) and H(C7)–Cl(3)). Although these ring hdyrogens were not located experimentally, the calculated H atom positions give H···Cl distances of which fall inside the van der Waals contact distance by 0.5 Å. The absence of significant ring puckering suggests some relatively strong *inter-* or *intramolecular* in-

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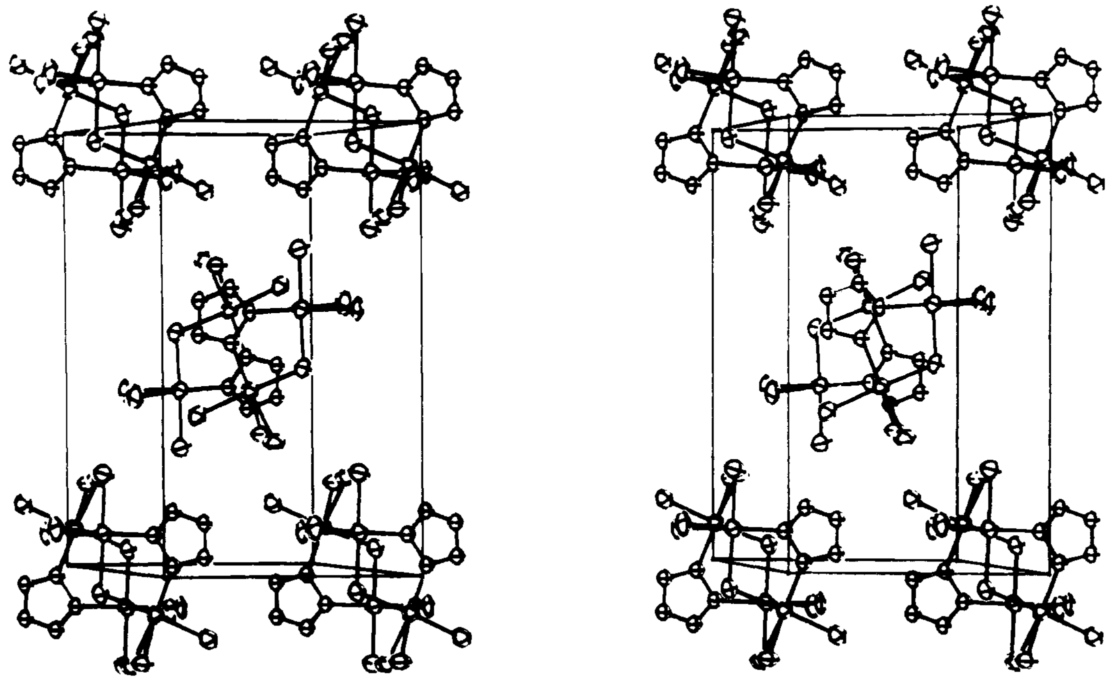

Figure 2. Stereoscopic view of packing in the unit cell. The *b* axis is vertical, the *c* axis is horizontal, and the *a* axis projects out of the page.

Table III. Atom Distances (Å) from Selected Best Planes

	plane							
atom	1	2	3	4	5	6	7	8
Pt(1)	0.0016 (8)[a]	0.0[a]	−3.0692 (7)	0.0007 (8)[a]	0.3283 (8)	0.0007 (8)[a]	−0.1725 (8)	0.0013 (8)[a]
Pt(2)	−0.0019 (8)[a]	3.0493 (8)	0.0[a]	0.1492 (8)	−0.0009 (8)[a]	0.0008 (8)[a]	0.0988 (8)	−0.0013 (8)[a]
Cl(1)	0.012 (7)[a]	2.287 (6)	−2.296 (5)	−0.026 (7)[a]	0.037 (7)[a]	−0.067 (7)[a]	−0.240 (7)	−0.068 (7)[a]
Cl(2)	−0.040 (5)[a]	−2.267 (6)	−3.946 (5)	−0.016 (6)[a]	0.581 (6)	0.030 (5)	−0.158 (6)	0.032 (5)[a]
Cl(3)	0.064 (6)[a]	3.868 (6)	2.275 (6)	0.399 (6)	0.032 (7)[a]	0.144 (6)	0.508 (7)	0.142 (6)[a]
N(1)	−0.19 (1)	−0.00 (1)	−1.17 (1)	−0.01 (1)[a]	0.21 (1)	−0.09 (1)[a]	−0.01 (1)[a]	−0.09 (1)[a]
N(2)	−0.27 (2)	1.14 (2)	0.00 (1)	−0.03 (2)	0.01 (2)[a]	−0.017 (2)[a]	0.02 (2)[a]	−0.17 (2)[a]
C(1)	0.85 (3)	0.0[a]	−4.97 (2)	0.67 (3)	1.11 (3)	0.75 (3)	0.32 (3)	0.75 (3)
C(2)	−0.57 (2)	0.0[a]	−4.99 (2)	−0.76 (2)	−0.32 (3)	−0.67 (2)	−1.10 (2)	−0.67 (2)
C(3)	0.93 (3)	4.96 (2)	0.0[a]	0.99 (3)	0.66 (3)	0.84 (3)	0.84 (3)	0.83 (3)
C(4)	−0.49 (3)	4.99 (2)	0.0[a]	−0.43 (3)	−0.77 (3)	−0.59 (3)	−0.57 (3)	−0.59 (3)
C(5)	−0.33 (2)	−1.06 (2)	−0.78 (2)	−0.06 (2)	0.23 (2)	−0.16 (2)	0.02 (2)[a]	−0.16 (2)[a]
C(6)	−0.56 (2)	−0.60 (3)	0.58 (2)	−0.18 (2)	−0.02 (3)	−0.34 (2)	0.00 (2)[a]	−0.34 (2)[a]
C(7)	−0.53 (2)	0.71 (2)	0.98 (2)	−0.17 (2)	−0.15 (2)	−0.36 (2)	−0.02 (2)[a]	−0.35 (2)[a]

[a] Atoms used for the calculation of the best plane.

Table IV. Dihedral Angles (Deg) between Selected Planes

	plane						
plane	1	2	3	4	5	6	7
2	85 (1)						
3	92 (1)	69.2 (7)					
4	5.3 (4)	86 (1)	87 (1)				
5	7.8 (4)	93 (1)	93 (1)	7.5 (4)			
6	3.4 (3)	87 (1)	90 (1)	2.7 (4)	5.7 (4)		
7	10.1 (6)	87 (1)	83 (2)	4.8 (7)	9.8 (6)	7.2 (6)	
8	3.4 (2)	87 (1)	90 (1)	2.7 (4)	5.6 (4)	0.1 (2)	7.2 (6)

teraction stabilizes the planar structure.

The pz ligand is planar as is normal for bridging pyrazolyl and pyrazolide groups. No significant differences in bond lengths compared to free pyrazole are observed.[9] The olefin-to-metal bonds appear normal when compared to other structural studies of platinum(II) olefin complexes.[10] The minimal lengthening of the olefin C–C bond (1.43 (4) vs. 1.337 (2) Å for free ethylene[11]) indicates limited evidence for $d\pi$–$p\pi$ back-bonding which is also in aggreement with other studies of simple olefin complexes.[12] The distance from Pt to the bridging Cl atom, the nonbridging Cl atom, and the ring nitrogen atoms are also in good agreement with available structural data for similar complexes.[10] With the exception of the olefin carbon atoms, the ligating atoms of the binuclear complex are essentially planar. For example, the dihedral angle between the ligation planes about the two platinum atoms is 7.5 (4)° (planes 4 and 5 in Table III). The dihedral angle between the pz ligand (plane 7, Table III) and the best plane through the central five-membered ring (plane 6, Table III) is 7.2 (6)°.

The molecular packing consists of columns of binuclear complexes stacked along the *x* direction. The angle between the normal to the best plane through the nonolefin atoms and the *a* axis is 17.5°. A three-dimensional packing diagram viewing the unit cell along the *a* axis is given in Figure 2. Within a given stack adjacent complexes are related by a center of symmetry. Adjacent pairs of molecules in a single

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stack may be weakly dimerized by van der Waals forces with the alternating distances between neighboring planar complexes in the stack being 3.77 (1) and 3.96 (1) Å (measured as the distance from the midpoint between the platinum atoms of one complex to the best plane of neighboring binuclear species, i.e., plane 8 in Table III).

Two different types of interaction might be invoked to rationalize the overall planarity of this complex. The weak van der Waals dimerization noted above may contribute to stabilization of the planar structure. This interaction appears not to involve direct metal–metal overlap since the shortest platinum–platinum distance between nearest-neighbor metal atoms in adjacent molecules in 4.028 (2) Å. The closest atom contact between the molecules occurs for the bridging ligands (Cl^- and the nitrogen atoms of pz) of nearest neighbors; however, this interaction is at a relatively long distance (3.74 (2) Å) compared to the sum of van der Waals radii for nitrogen and chlorine. Thus on balance, this interaction appears to be relatively weak and probably is not the sole driving force for planarity. The second type of interaction favoring planarity involves the potential of the pyrazolide ligand to function as a *π-donor* group via the filled π orbitals of the ring. As noted above, the platinum-to-carbon and -nitrogen bond distances are not significantly shorter than those of other related complexes; therefore, strong structural support for this type of interaction is lacking. We have, however, observed that the barrier to olefin rotation is higher in the title complex[13] than in the mononuclear species *trans*-$PtCl_2(C_2H_4)(C_3H_4N_2)$. The higher barrier to olefin rotation in the binuclear complex may indicate a synergistic enhancement of the platinum-olefin π bond due to ligand-to-metal π donation by the pyrazolide group.

Acknowledgment. We would like to acknowledge valuable discussions with Paul Swepston, financial assistance in the form of a fellowship by the Phillips Petroleum Co. (W.C.D.), and support of the computing aspects of this research by the University of Arkansas Research Reserve Committee.

Registry No. $(C_2H_4)(Cl)Pt(\mu\text{-}Cl)(\mu\text{-}C_3H_3N_2)Pt(Cl)(C_2H_4)$, 76648-29-8.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and a table of final thermal parameters (7 pages). Ordering information is given on any current masthead page.

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[13] Johnson, D. A.; Deese, W. C., unpublished results.

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973,
and the Department of Chemistry, Georgetown University, Washington, D.C. 20007

Crystal and Molecular Structures of Pentaammine(pyrazine)ruthenium(II) Tetrafluoroborate and Pentaammine(pyrazine)ruthenium(III) Trifluoromethanesulfonate Monohydrate

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For $[Ru(NH_3)_5(C_4N_2H_4)](BF_4)_2$ the space group is $P2_12_12_1$ with cell parameters a = 12.615 (2) Å, b = 15.610 (3) Å, c = 7.965 (2) Å, and Z = 4. For $[Ru(NH_3)_5(C_4N_2H_4)](CF_3SO_3)_3{\cdot}H_2O$ the space group is *Pnma* with cell parameters a = 23.795 (4) Å, b = 8.062 (2) Å, c = 12.848 (2) Å, and Z = 4. The geometries of both the $Ru(NH_3)_5pz^{2+}$ (pz = pyrazine) and $Ru(NH_3)_5pz^{3+}$ cations are approximately octahedral, with the plane of the pyrazine ring intersecting at a 45° angle the equatorial plane containing the bound pyrazine N and the three N atoms of the NH_3 groups, as is expected from steric considerations. The $Ru{-}NH_3$ bond lengths are similar to those found in other ammine complexes: $Ru(II){-}NH_3$, 2.15–2.17 Å; $Ru(III){-}NH_3$, 2.10–2.13 Å. By contrast the Ru(II)–pz bond (2.006 Å) is shorter than the Ru(III)–pz bond (2.076 Å) by 0.07 Å. This is attributed to π back-bonding between Ru(II) and pyrazine. The dimensions of the mononuclear ions $Ru(NH_3)_5pz^{2+}$ and $Ru(NH_3)_5pz^{3+}$ are used to model the structure of valence-localized $Ru^{II}(NH_3)_5pzRu^{III}(NH_3)_5^{5+}$. The observed properties of this ion are then compared with those predicted from Marcus–Hush electron-transfer theory.

Introduction

Although the physical and chemical properties of mononuclear pentaammineruthenium(II) and -(III) complexes containing aromatic N heterocycles ($Ru(NH_3)_5L^{2+}$ and $Ru(NH_3)_5L^{3+}$, L = pyridine, isonicotinamide, pyrazine, etc.), have been extensively investigated,[1-6] no structural data have been available for complexes of this class. It is especially desirable to compare bond length data for $Ru(NH_3)_5L^{2+}$ and $Ru(NH_3)_5L^{3+}$ with the same π acid L. This comparison is expected to provide additional information concerning the back-bonding interaction between L and the π base $Ru(NH_3)_5{}^{2+}$, which is manifested in the thermodynamic[4,5] and spectral[1,6] properties of $Ru(NH_3)_5L^{2+}$. Furthermore, the magnitudes of the bond lengths for such complexes in both oxidation states are of considerable interest in assessing the success of current electron-transfer theories. Biomolecular self-exchange rates for $Ru(NH_3)_5L^{2+}/Ru(NH_3)_5L^{3+}$ couples have now been experimentally evaluated[7] and can be compared with theoretical values if the dimensions of the ions are known.[8-10] Structural data bearing on the bond length differences between $Ru(NH_3)_5L^{2+}$ and $Ru(NH_3)_5L^{3+}$ are also of importance in the area of intramolecular-electron-transfer theory as studied through the physical properties of valence-trapped mixed-valence ions,[11] e.g., the series of mixed-valence

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