ane)]$^{3+}$, 70304-28-8; [(NH$_3$)$_5$RuS(CH$_2$)$_4$SH]$^{2+}$, 70288-20-9; [(NH$_3$)$_5$RuS(CH$_2$)$_3$SH]$^{2+}$, 70288-21-0; [(NH$_3$)$_5$RuSC$_6$H$_5$](PF$_6$)$_2$, 70288-23-2; [(NH$_3$)$_5$RuSeC$_6$H$_5$](PF$_6$)$_2$, 70288-25-4; [(NH$_3$)$_5$RuS(CH$_3$)$_2$]$^{3+}$, 69204-65-5; [(NH$_3$)$_5$RuS(H)(CH$_2$)$_4$SH]$^{2+}$, 70288-26-5; [(NH$_3$)$_5$RuOH$_2$](PF$_6$)$_2$, 34843-18-0; [(NH$_3$)$_5$RuCl]Cl$_2$, 18532-87-1; diphenyl disulfide, 882-33-7; diphenyl diselenide, 1666-13-3.

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# Crystal Structures of *cis*-Tetraamminebis(isonicotinamide)ruthenium(II) and -(III) Perchlorates

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Single crystals of *cis*-[Ru(NH$_3$)$_4$(isn)$_2$](ClO$_4$)$_3$·H$_2$O (I) and *cis*-[Ru(NH$_3$)$_4$(isn)$_2$](ClO$_4$)$_2$ (II) (isn = isonicotinamide) have been studied by X-ray structural analysis. Both I and II crystallize in the centrosymmetric monoclinic space group $P2_1/n$. For I, $a$ = 15.337 (15) Å, $b$ = 10.636 (8) Å, $c$ = 17.467 (16) Å, $\beta$ = 110.78 (7)°, $V$ = 2264 (4) Å$^3$, and $\rho$(calcd) = 1.82 g cm$^{-3}$ for $Z$ = 4 and mol wt 729.82. For II, $a$ = 12.206 (4) Å, $b$ = 23.986 (15) Å, $c$ = 7.749 (2) Å, $\beta$ = 93.88 (3)°, $V$ = 2264 (2) Å$^3$, and $\rho$(calcd) = 1.80 g cm$^{-3}$ for $Z$ = 4 and mol wt 612.35. Diffraction data for 0.6° < 2$\theta$ < 45° (Mo K$\bar{\alpha}$ radiation) were collected on a Syntex $P2_1$ automated diffractometer. The structures were solved by the usual Patterson, Fourier, and least-squares refinement techniques. In both solutions, all atoms other than hydrogen were located directly. The structure of I was refined to $R_F$ = 4.7% and $R_{wF}$ = 6.5% for the 3080 reflections with $F_o^2 > 3\sigma(F_o)^2$. The structure of II was refined to $R_F$ = 4.8% and $R_{wF}$ = 6.4% for 2246 reflections. The weighted means for Ru$^{III}$–NH$_3$ and axial Ru$^{II}$–NH$_3$ bond distances are 2.125 (7) and 2.143 (5) Å, respectively. The Ru–NH$_3$ bond distances for the ammonias trans to isonicotinamides in II are consistently longer (weighted mean 2.170 (6) Å) than the axial distances, and a statistical analysis indicates that a small trans influence is present for II. The weighted means for Ru$^{III}$–N(isn) and Ru$^{II}$–N(isn) bond lengths are 2.099 (4) and 2.060 (4) Å. The decrease in Ru–N(isn) bond length for the Ru(II) state is attributed to d$\pi$–$\pi$* interactions.

## Introduction

Crystallographic metal–ligand distances have been used to estimate the contribution of the inner-sphere reorganization energy to the activation energy of electron-transfer reactions.[1] Such calculations also require a knowledge of the force constants for the relevant metal–ligand bonds.[1-3] As the difference in metal–ligand distances for the two oxidation states involved in a self-exchange process decreases, the free energy of activation due to inner-sphere reorganization ($\Delta G_i^*$) becomes smaller if the force constants are assumed to be unchanged. Thus, the increased rate of self-exchange for [Fe(phen)$_3$]$^{2+/3+}$ [4] over [Fe(H$_2$O)$_6$]$^{2+/3+}$ is thought to be due in part to the small difference between the Fe$^{II}$–N and Fe$^{III}$–N distances in the former case.[1] The remainder of the difference in rates is accounted for by the solvent ($\Delta G_o^*$) and electrostatic work ($w_e$) contributions to the overall activation energy for self-exchange if the reactions are adiabatic.

Ruthenium provides especially attractive self-exchange systems for testing theoretical expressions of the above type. In many cases, reduction of a ruthenium(III) complex to the ruthenium(II) state does not introduce excessive liability to the ion, thus making possible accurate determinations of self-exchange rates for many closely related systems. Such a series is that in which the ammonias of [Ru(NH$_3$)$_6$]$^{n+}$ ($n$ = 2, 3) are successively replaced with $\pi$ acids.

Stynes and Ibers[5] have determined the molecular structures of [Ru(NH$_3$)$_6$]I$_2$ and [Ru(NH$_3$)$_6$](BF$_4$)$_3$ and conclude that the inner-sphere distortion necessary to form the activated complex can be attained easily at room temperature. Brown and Sutin[6] have suggested that $\Delta G_i^*$ is small in comparison to the $\Delta G_o^*$ term for ruthenium(II) and -(III) self-exchange. They propose that the large increase in self-exchange rate on going from [Ru(NH$_3$)$_6$]$^{2+/3+}$ to [Ru(bpy)$_3$]$^{2+/3+}$ (a factor of approximately 10$^5$) is primarily due to the change in the radii of the cations rather than to a decrease in $\Delta G_i^*$.

If the term $\Delta G_i^*$ is to be accurately estimated from theoretical expressions for the series [Ru(NH$_3$)$_6$]$^{2+/3+}$, [Ru(NH$_3$)$_5$L]$^{2+/3+}$, [Ru(NH$_3$)$_4$L$_2$]$^{2+/3+}$, ..., [RuL$_6$]$^{2+/3+}$ (L = $\pi$ acceptor such as py, isn, or pyz), then accurate molecular dimensions must be known. Preliminary results of Wells and Creutz[7] for the complexes [Ru(NH$_3$)$_5$pyz](BF$_4$)$_2$ and [Ru(NH$_3$)$_5$pyz](CF$_3$SO$_3$)$_3$ indicate that there is a substantially shorter Ru–N(pyz) distance in the ruthenium(II) complex. We have determined the crystal structures of *cis*-[Ru(NH$_3$)$_4$(isn)$_2$](ClO$_4$)$_2$ and *cis*-[Ru(NH$_3$)$_4$(isn)$_2$](ClO$_4$)$_3$·H$_2$O to observe the effect of two $\pi$ acceptors on the molecular dimensions.

Crystal structures have also proven useful in demonstrating the presence of back-bonding in ruthenium(II) complexes with $\pi$-acceptor ligands. In such cases the metal-ligand bond length is significantly less for the $\pi$-acceptor ligand than for a ligand with the same donor atom but no $\pi$-acceptor capability. The effect has been clearly observed in [Ru(NH$_3$)$_5$NO$_2$]Cl,[8] [Ru(NH$_3$)$_5$NO]Cl$_2$,[9] [Ru(OH)(NH$_3$)$_4$NO]Cl$_2$,[9] [(Ru(NH$_3$)$_5$)$_2$N$_2$](BF$_4$)$_2$,[10] and [(Ru(py)$_4$)$_2$C$_2$O$_4$](BF$_4$)$_2$,[11] where NO$_2^-$, NO$^+$, N$_2$, and pyridine are believed to participate in d$\pi$–$\pi$* bonding interactions. In some of the above compounds, a trans influence is observed;[8,10] that is, the ligands coaxial

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**Table I.** Summary of Crystal Data, Intensity Collection, and Structure Refinement of *cis*-$[Ru(NH_3)_4(isn)_2](ClO_4)_3 \cdot H_2O$ and *cis*-$[Ru(NH_3)_4(isn)_2](ClO_4)_2$

| | Ru(III) | Ru(II) |
|---|---|---|
| formula | $RuCl_{12}H_{26}N_8O_{15}Cl_3$ | $RuC_{12}H_{24}N_8O_{12}Cl_2$ |
| *a*, Å | 15.337 (15) | 12.206 (4) |
| *b*, Å | 10.636 (8) | 23.986 (15) |
| *c*, Å | 17.467 (16) | 7.749 (2) |
| $\beta$, deg | 110.78 (7) | 93.88 (3) |
| cryst system | monoclinic | monoclinic |
| *V*, Å$^3$ | 2264 (4) | 2264 (2) |
| *Z* | 4 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.82 | 1.80 |
| $\rho_{obsd}$, g/cm$^3$ [a] | 1.81 | 1.79 |
| space group | $P2_1/n$ | $P2_1/n$ |
| cryst faces and dimens (from centroid in mm) | $(11\bar{1})$, 0.125; $(\bar{1}\bar{1}1)$, 0.125; $(1\bar{1}\bar{1})$, 0.125; $(\bar{1}11)$, 0.125; $(\bar{1}01)$, 0.125; (001), 0.130; $(00\bar{1})$, 0.130 | (010), 0.060; $(0\bar{1}0)$, 0.060; (101), 0.097; $(\bar{1}0\bar{1})$, 0.097; $(10\bar{1})$, 0.115; $(\bar{1}01)$, 0.115 |
| radiation[b] | Mo K$\bar{\alpha}$ ($\lambda$ 0.710 69 Å) | Mo K$\bar{\alpha}$ ($\lambda$ 0.710 69 Å) |
| abs coeff ($\mu$), cm$^{-1}$ | 9.63 | 9.84 |
| takeoff angle, deg | 3.0 | 3.0 |
| scan speed, deg/min | 2.0 to 29.3 ($\theta/2\theta$ scans) | 2.0 to 29.3 ($\theta/2\theta$ scans) |
| scan range, deg | 1.0 below K$\alpha_1$ to 1.0 above K$\alpha_1$ | 1.0 below K$\alpha_1$ to 1.0 above K$\alpha_1$ |
| bkgd/scan time ratio | 0.25 | 0.25 |
| data collected | $2\theta$ of 0.6 to 45°, $\pm hkl$ | $2\theta$ of 0.6 to 45°, $h,k,\pm l$ |
| unique averaged data ($F_o^2 > 3\sigma(F_o)^2$) | 3080 | 2246 |
| no. of variables | 352 | 298 |
| error in obsn of unit wt | 1.74 | 1.81 |
| $R_F$, % | 4.7 | 4.8 |
| $R_{wF}$, % | 6.2 | 6.4 |

[a] Determined by flotation in $CH_2I_2$ and $CCl_4$. [b] Mosaic graphite monochromator.

with the $\pi$ acceptor are displaced to longer than normal metal–ligand distances. Comparison to analogous complexes of metals unable to strongly back-bond (e.g., Co(III))[12,13] supports the contention that the relevant bond distances are useful for identifying $\pi$ interactions qualitatively and estimating the magnitude of the effects. In addition to structural evidence, there is also substantial chemical and physical evidence for back-bonding in ruthenium(II)–$\pi$-acid complexes.[14–17]

## Experimental Section

The compounds *cis*-$[Ru(NH_3)_4(isn)_2](ClO_4)_3 \cdot H_2O$ (compound I) and *cis*-$[Ru(NH_3)_4(isn)_2](ClO_4)_2$ (II) were prepared as described previously.[18] Crystals suitable for X-ray analysis were obtained by crystallization from saturated solution by using 0.1 M $HClO_4$ as the solvent.

**Crystal Data.** Compound I crystallized as orange hexagonal prisms with unequally developed faces. A suitable crystal with seven faces was selected for data collection. Compound II crystallized as needles with rectangular cross sections. The crystals appeared yellow-green by reflected light and deep red by transmitted light. A long needle was cleaved to obtain a parallelepiped of suitable size for data collection. The crystals were each mounted on a glass fiber with epoxy cement so that the longest crystal dimension was approximately parallel to the fiber axis. The crystal faces and dimensions are given in Table I.

Data were collected on a Syntex $P2_1$ four-circle diffractometer by using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Least-squares refinement of the setting angles of 15 machine-centered reflections yielded the crystal system and unit cell dimensions (Table I). From the systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) both crystals were found to belong uniquely to the space group $P2_1/n$, with four molecules per unit cell.

**Data Collection and Reduction.** Examination of the $\omega$ scans of several low-angle centered reflections showed no defects in the crystals. Full peak widths at half-height were less than 0.2° for both crystals. Intensity data were collected by using variable-speed $2\theta$–$\theta$ scans. Data collection parameters are given in Table I. Three standards were monitored every 40 reflections. Neither crystal exhibited any significant change in the intensities of the standard reflections. Corrections were made for background, Lorentz–polarization effects, and absorption.[19]

**Structure Solution and Refinement.** The coordinates of the ruthenium atoms were determined from a three-dimensional Patterson map. The positions of the other nonhydrogen atoms were determined from subsequent difference Fourier maps. Hydrogen atoms (located or idealized) were not included in the structure factor calculations. Anisotropic full-matrix least-squares refinement of all the nonhydrogen coordinates gave the final values of $R_F$, $R_{wF}$, and the error in an observation of unit weight shown in Table I. A final difference Fourier map showed no maxima greater than 0.75 (I) and 0.73 e/Å$^3$ (II). Carbon atom peaks were 4.4 e/Å$^3$ or larger for both I and II. Positional and thermal parameters for the cations are listed in Table II. Listings of observed and calculated structure factors (×10) and root-mean-square amplitudes of thermal vibration are available as supplementary material.

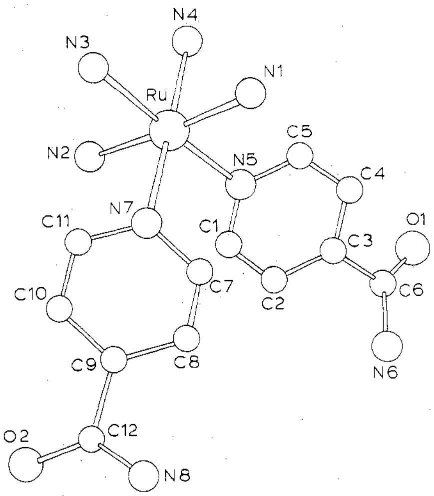

**Figure 1.** Atom numbering scheme for the cations of I and II. The structure shown is that of I. The cation of II is almost identical with the exception that N(6) and O(1) exchange positions.

## Results and Discussion

**Structural Description of $[Ru(NH_3)_4(isn)_2](ClO_4)_3 \cdot H_2O$ (I).** The atom-numbering scheme of an isolated cation is shown in Figure 1 and a stereoview is given in Figure 2. Note that the unit cell contains two enantiomeric pairs, but only one isomer is shown in Figures 1 and 2. The bond distances, bond angles, and dihedral angles are given in Tables III, IV, and V.

**Table II.** Positional and Thermal Parameters[a]

| atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| *cis*-$[Ru(NH_3)_4(isn)_2]^{3+}$ Ion | | | | | | | | | |
| Ru(1) | 0.96125 (6) | 0.15962 (5) | 0.21290 (3) | 1.98 (2) | 1.77 (2) | 2.45 (2) | −0.02 (2) | 0.52 (1) | 0.00 (2) |
| O(1) | 1.4289 (3) | −0.0395 (5) | 0.3684 (4) | 2.8 (2) | 3.8 (2) | 6.6 (3) | −0.8 (2) | −1.2 (2) | 0.3 (2) |
| O(2) | 0.9910 (4) | 0.8073 (4) | 0.3016 (3) | 5.9 (2) | 2.1 (2) | 4.4 (2) | −0.1 (2) | 1.1 (2) | 0.4 (2) |
| N(1) | 0.9445 (4) | 0.0849 (5) | 0.3188 (3) | 3.5 (2) | 2.9 (2) | 2.5 (2) | −0.3 (2) | 0.7 (2) | 0.4 (2) |
| N(2) | 0.9711 (4) | 0.2286 (5) | 0.1022 (3) | 3.5 (2) | 2.2 (2) | 3.2 (2) | 0.2 (2) | 1.6 (1) | 0.4 (2) |
| N(3) | 0.8141 (4) | 0.1801 (6) | 0.1638 (4) | 2.1 (2) | 3.2 (3) | 4.3 (3) | 0.2 (2) | 0.3 (2) | 0.5 (2) |
| N(4) | 0.9456 (4) | −0.0222 (5) | 0.1609 (3) | 3.4 (2) | 2.2 (2) | 3.1 (2) | −0.5 (2) | 1.1 (2) | −0.7 (2) |
| N(5) | 1.1065 (3) | 0.1315 (5) | 0.2620 (3) | 2.1 (2) | 1.9 (2) | 2.8 (2) | 0.1 (2) | −0.7 (1) | 0.3 (2) |
| N(6) | 1.4560 (4) | 0.1650 (7) | 0.4021 (4) | 2.7 (2) | 4.6 (3) | 4.9 (3) | 0.4 (2) | −0.6 (2) | 0.5 (3) |
| N(7) | 0.9767 (3) | 0.3420 (5) | 0.2608 (3) | 2.4 (2) | 2.0 (2) | 2.6 (2) | 0.4 (2) | 0.7 (1) | 0.2 (2) |
| N(8) | 1.0543 (6) | 0.7380 (7) | 0.4312 (4) | 9.3 (5) | 3.4 (3) | 3.5 (3) | 0.2 (3) | 0.4 (3) | −1.0 (3) |
| C(1) | 1.1661 (4) | 0.2190 (7) | 0.2552 (4) | 2.2 (2) | 2.7 (3) | 3.4 (3) | 0.2 (2) | −0.9 (2) | 0.3 (3) |
| C(2) | 1.2619 (4) | 0.2035 (7) | 0.2898 (4) | 2.5 (2) | 2.8 (3) | 3.1 (2) | −0.1 (2) | −1.1 (2) | 0.0 (2) |
| C(3) | 1.2977 (4) | 0.0930 (6) | 0.3313 (4) | 2.5 (2) | 2.7 (3) | 2.2 (2) | −0.2 (2) | −0.7 (2) | 0.7 (2) |
| C(4) | 1.2358 (4) | 0.0007 (7) | 0.3364 (4) | 2.5 (2) | 2.7 (3) | 3.4 (3) | −0.2 (2) | −1.0 (2) | 0.4 (2) |
| C(5) | 1.1414 (4) | 0.0230 (6) | 0.3011 (4) | 3.0 (2) | 2.3 (3) | 2.9 (2) | −0.5 (2) | −0.9 (2) | 0.2 (2) |
| C(6) | 1.4004 (4) | 0.0674 (7) | 0.3697 (4) | 2.5 (2) | 3.0 (3) | 3.7 (3) | −0.3 (2) | −1.2 (2) | 0.3 (3) |
| C(7) | 1.0408 (5) | 0.3686 (6) | 0.3350 (4) | 3.1 (2) | 2.8 (3) | 2.4 (2) | 0.3 (2) | 0.8 (2) | 0.2 (2) |
| C(8) | 1.0560 (4) | 0.4887 (7) | 0.3675 (4) | 3.1 (2) | 2.4 (3) | 3.0 (2) | 0.2 (2) | 1.0 (2) | 0.1 (2) |
| C(9) | 1.0018 (4) | 0.5865 (6) | 0.3219 (4) | 2.9 (2) | 2.1 (3) | 3.5 (2) | −0.3 (2) | 1.7 (2) | −0.1 (2) |
| C(10) | 0.9356 (4) | 0.5595 (6) | 0.2456 (4) | 3.1 (2) | 2.4 (3) | 3.2 (3) | 0.2 (2) | 1.0 (2) | 0.5 (2) |
| C(11) | 0.9243 (5) | 0.4378 (6) | 0.2172 (4) | 3.1 (2) | 2.1 (3) | 3.2 (3) | 0.3 (2) | 0.7 (2) | 0.4 (2) |
| C(12) | 1.0154 (5) | 0.7214 (7) | 0.3508 (5) | 4.2 (3) | 2.3 (3) | 3.7 (3) | −0.2 (3) | 1.3 (2) | −0.2 (3) |
| *cis*-$[Ru(NH_3)_4(isn)_2]^{2+}$ Ion | | | | | | | | | |
| Ru(1) | 0.67744 (6) | 0.38654 (3) | 0.27103 (8) | 2.14 (2) | 2.07 (2) | 2.10 (2) | 0.23 (3) | 0.11 (2) | −0.15 (3) |
| O(1) | 1.1621 (6) | 0.2298 (3) | 0.3285 (10) | 3.7 (3) | 3.7 (3) | 9.5 (4) | 0.9 (3) | 0.1 (3) | 1.2 (3) |
| O(2) | 0.3724 (5) | 0.1394 (3) | 0.2824 (8) | 2.9 (3) | 3.7 (3) | 5.2 (3) | −1.3 (2) | 0.3 (3) | −0.4 (3) |
| N(1) | 0.6800 (6) | 0.3935 (3) | 0.5465 (8) | 2.7 (3) | 4.8 (4) | 2.1 (3) | 0.2 (3) | 0.4 (2) | −0.6 (3) |
| N(2) | 0.6712 (6) | 0.3816 (3) | 0.0060 (8) | 3.7 (3) | 3.2 (3) | 2.1 (3) | 0.0 (3) | 0.4 (3) | −0.1 (3) |
| N(3) | 0.5145 (6) | 0.4234 (3) | 0.2577 (9) | 2.2 (3) | 3.5 (3) | 4.2 (3) | 1.3 (3) | −0.3 (3) | −0.2 (3) |
| N(4) | 0.7430 (6) | 0.4697 (3) | 0.2487 (10) | 3.6 (3) | 2.3 (3) | 4.4 (3) | −0.2 (3) | −0.4 (3) | 0.1 (3) |
| N(5) | 0.8339 (5) | 0.3558 (3) | 0.2864 (8) | 2.6 (3) | 1.8 (3) | 2.0 (2) | −0.4 (2) | 0.6 (2) | −0.1 (2) |
| N(6) | 1.2422 (6) | 0.3125 (4) | 0.3933 (12) | 2.5 (3) | 5.3 (4) | 7.3 (5) | −0.2 (4) | −0.4 (4) | −0.6 (4) |
| N(7) | 0.6125 (5) | 0.3072 (3) | 0.2915 (8) | 1.8 (3) | 2.3 (3) | 2.4 (3) | 0.2 (2) | 0.0 (2) | 0.3 (2) |
| N(8) | 0.5300 (7) | 0.1001 (3) | 0.3812 (11) | 4.2 (4) | 3.2 (4) | 6.3 (4) | −0.2 (3) | −1.0 (4) | 1.5 (3) |
| C(1) | 0.8583 (6) | 0.3070 (3) | 0.2845 (10) | 2.2 (3) | 2.3 (3) | 3.0 (3) | 0.1 (3) | 0.7 (3) | 0.0 (3) |
| C(2) | 0.9615 (6) | 0.2812 (3) | 0.2269 (10) | 2.1 (3) | 2.8 (3) | 2.7 (3) | −0.2 (3) | 0.4 (3) | 0.6 (3) |
| C(3) | 1.0455 (6) | 0.3088 (3) | 0.3249 (10) | 2.3 (3) | 3.2 (4) | 2.1 (3) | −0.1 (3) | 0.8 (3) | 0.7 (3) |
| C(4) | 1.0237 (7) | 0.3601 (4) | 0.3996 (10) | 2.3 (4) | 2.8 (3) | 2.5 (3) | 0.0 (3) | 0.3 (3) | −0.1 (3) |
| C(5) | 0.9188 (7) | 0.3814 (3) | 0.3802 (10) | 2.8 (4) | 2.5 (3) | 2.6 (3) | −0.6 (3) | −0.0 (3) | 0.6 (3) |
| C(6) | 1.1550 (8) | 0.2800 (4) | 0.3521 (11) | 3.6 (4) | 3.0 (4) | 3.3 (4) | 0.9 (4) | 0.8 (3) | 0.9 (3) |
| C(7) | 0.6616 (7) | 0.2681 (3) | 0.3932 (10) | 2.5 (4) | 3.0 (4) | 2.7 (3) | −0.3 (3) | 0.4 (3) | 0.3 (3) |
| C(8) | 0.6238 (7) | 0.2137 (4) | 0.4038 (10) | 2.7 (4) | 3.9 (4) | 2.2 (3) | −0.2 (3) | 0.5 (3) | 0.3 (3) |
| C(9) | 0.5236 (7) | 0.1996 (3) | 0.3128 (10) | 2.5 (3) | 2.5 (3) | 2.0 (3) | −0.2 (3) | 0.6 (3) | 0.0 (3) |
| C(10) | 0.4721 (7) | 0.2403 (3) | 0.2098 (10) | 2.7 (4) | 2.8 (3) | 2.8 (3) | 0.2 (3) | 0.3 (3) | −0.4 (3) |
| C(11) | 0.5170 (7) | 0.2926 (4) | 0.1987 (10) | 3.0 (4) | 3.2 (4) | 2.2 (3) | 0.5 (3) | 0.1 (3) | −0.1 (3) |
| C(12) | 0.4784 (7) | 0.1431 (4) | 0.3256 (10) | 2.5 (4) | 3.9 (4) | 2.3 (3) | −0.8 (3) | 0.6 (3) | −0.3 (3) |

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*\cdot c^*)]$.

**Table III.** Intramolecular Bond Lengths (Å) for I and II with Esd's

| atoms | I | II | atoms | I | II |
|---|---|---|---|---|---|
| Ru-N(1) | 2.111 (4) | 2.140 (5) | C(8)-C(9) | 1.392 (8) | 1.411 (9) |
| Ru-N(2) | 2.124 (5) | 2.146 (7) | C(9)-C(10) | 1.389 (8) | 1.385 (9) |
| Ru-N(3) | 2.122 (4) | 2.173 (7) | C(10)-C(11) | 1.375 (8) | 1.373 (9) |
| Ru-N(4) | 2.144 (4) | 2.160 (11) | C(9)-C(12) | 1.511 (8) | 1.510 (9) |
| Ru-N(5) | 2.105 (4) | 2.044 (6) | C(12)-O(2) | 1.220 (7) | 1.223 (8) |
| Ru-N(7) | 2.093 (4) | 2.072 (5) | C(12)-N(8) | 1.328 (8) | 1.317 (9) |
| N(5)-C(1) | 1.340 (7) | 1.372 (21) | Cl(1)-O(3) | 1.412 (5) | 1.400 (6) |
| N(5)-C(5) | 1.351 (6) | 1.371 (8) | Cl(1)-O(4) | 1.413 (6) | 1.403 (6) |
| C(1)-C(2) | 1.387 (7) | 1.405 (15) | Cl(1)-O(5) | 1.409 (5) | 1.444 (8) |
| C(2)-C(3) | 1.387 (7) | 1.399 (23) | Cl(1)-O(6) | 1.372 (6) | 1.400 (7) |
| C(3)-C(4) | 1.391 (7) | 1.393 (9) | Cl(2)-O(7) | 1.431 (6) | 1.420 (6) |
| C(4)-C(5) | 1.378 (7) | 1.379 (10) | Cl(2)-O(8) | 1.349 (7) | 1.417 (6) |
| C(3)-C(6) | 1.507 (7) | 1.506 (37) | Cl(2)-O(9) | 1.351 (7) | 1.428 (6) |
| C(6)-O(1) | 1.221 (6) | 1.223 (198) | Cl(2)-O(10) | 1.344 (6) | 1.395 (6) |
| C(6)-N(6) | 1.335 (7) | 1.341 (53) | Cl(3)-O(11) | 1.415 (5) | |
| N(7)-C(7) | 1.351 (7) | 1.341 (25) | Cl(3)-O(12) | 1.374 (5) | |
| N(7)-C(11) | 1.352 (7) | 1.373 (24) | Cl(3)-O(13) | 1.369 (6) | |
| C(7)-C(8) | 1.384 (8) | 1.387 (9) | Cl(3)-O(14) | 1.388 (7) | |

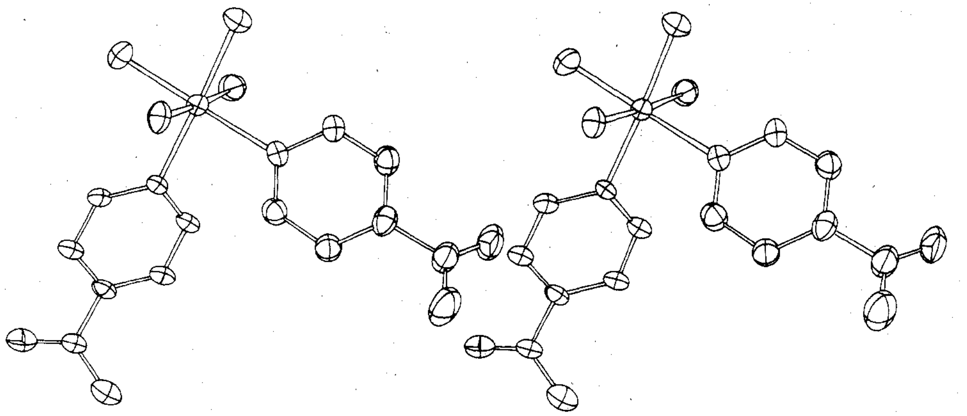

**Figure 2.** Stereoscopic view of $[Ru(NH_3)_4(isn)_2]^{3+}$ (cation of I, 50% thermal probability ellipsoids).

**Table IV.** Bond Angles (deg) for I and II

| atoms | I | II |
|---|---|---|
| N(1)-Ru-N(2) | 176.64 (17) | 178.26 (22) |
| N(3)-Ru-N(5) | 177.70 (16) | 177.10 (21) |
| N(4)-Ru-N(7) | 178.13 (18) | 179.24 (48) |
| N(1)-Ru-N(3) | 90.32 (19) | 88.11 (21) |
| N(1)-Ru-N(4) | 87.17 (19) | 91.60 (38) |
| N(1)-Ru-N(5) | 90.09 (18) | 91.12 (21) |
| N(1)-Ru-N(7) | 91.69 (17) | 88.54 (105) |
| N(2)-Ru-N(3) | 91.72 (18) | 90.28 (24) |
| N(2)-Ru-N(4) | 90.32 (19) | 87.68 (22) |
| N(2)-Ru-N(5) | 87.63 (18) | 90.46 (20) |
| N(2)-Ru-N(7) | 90.74 (17) | 92.17 (77) |
| N(3)-Ru-N(4) | 90.51 (19) | 87.89 (25) |
| N(3)-Ru-N(7) | 91.08 (17) | 91.37 (49) |
| N(4)-Ru-N(5) | 89.29 (16) | 89.34 (23) |
| N(5)-Ru-N(7) | 90.90 (18) | 91.40 (48) |
| Ru-N(5)-C(1) | 121.43 (39) | 120.77 (51) |
| Ru-N(5)-C(5) | 120.03 (36) | 122.56 (42) |
| N(5)-C(1)-C(2) | 121.96 (50) | 122.63 (111) |
| C(1)-C(2)-C(3) | 119.40 (49) | 118.45 (63) |
| C(2)-C(3)-C(4) | 118.60 (47) | 119.34 (146) |
| C(3)-C(4)-C(5) | 118.87 (51) | 119.01 (61) |
| C(4)-C(5)-N(5) | 122.57 (50) | 123.64 (66) |
| C(5)-N(5)-C(1) | 118.55 (44) | 116.65 (58) |
| C(2)-C(3)-C(6) | 123.00 (50) | 118.02 (261) |
| C(4)-C(3)-C(6) | 118.39 (49) | 122.58 (384) |
| C(3)-C(6)-O(1) | 119.09 (51) | 120.10 (220) |
| C(3)-C(6)-N(6) | 117.37 (49) | 116.77 (745) |
| N(6)-C(6)-O(1) | 123.53 (53) | 123.03 (542) |
| Ru-N(7)-C(7) | 121.18 (38) | 121.99 (138) |
| Ru-N(7)-C(11) | 120.91 (37) | 120.64 (146) |
| N(7)-C(7)-C(8) | 123.10 (48) | 123.69 (84) |
| C(7)-C(8)-C(9) | 118.40 (50) | 118.49 (60) |
| C(8)-C(9)-C(10) | 118.70 (50) | 117.61 (58) |
| C(9)-C(10)-C(11) | 119.69 (50) | 120.80 (60) |
| C(10)-C(11)-N(7) | 122.21 (50) | 121.88 (86) |
| C(11)-N(7)-C(7) | 117.89 (46) | 117.37 (54) |
| C(8)-C(9)-C(12) | 122.30 (51) | 123.01 (59) |
| C(10)-C(9)-C(12) | 118.95 (51) | 119.37 (58) |
| C(9)-C(12)-O(2) | 120.27 (54) | 117.60 (65) |
| C(9)-C(12)-N(8) | 115.94 (54) | 119.61 (63) |
| N(8)-C(12)-O(2) | 123.79 (57) | 122.78 (67) |
| O(3)-Cl(1)-O(4) | 106.78 (34) | 111.69 (40) |
| O(3)-Cl(1)-O(5) | 110.79 (36) | 105.99 (50) |
| O(3)-Cl(1)-O(6) | 108.63 (48) | 113.84 (42) |
| O(4)-Cl(1)-O(5) | 108.99 (39) | 106.63 (49) |
| O(4)-Cl(1)-O(6) | 112.69 (53) | 112.38 (50) |
| O(5)-Cl(1)-O(6) | 108.95 (37) | 105.63 (65) |
| O(7)-Cl(2)-O(8) | 110.48 (54) | 108.47 (42) |
| O(7)-Cl(2)-O(9) | 107.09 (57) | 111.24 (44) |
| O(7)-Cl(2)-O(10) | 108.40 (39) | 111.48 (38) |
| O(8)-Cl(2)-O(9) | 106.48 (71) | 105.37 (40) |
| O(8)-Cl(2)-O(10) | 112.73 (56) | 109.49 (35) |
| O(9)-Cl(2)-O(10) | 111.53 (57) | 110.58 (37) |
| O(11)-Cl(3)-O(12) | 110.41 (37) | |
| O(11)-Cl(3)-O(13) | 114.13 (44) | |
| O(11)-Cl(3)-O(14) | 106.52 (50) | |
| O(12)-Cl(3)-O(13) | 113.22 (44) | |
| O(12)-Cl(3)-O(14) | 108.56 (55) | |
| O(13)-Cl(3)-O(14) | 103.39 (57) | |

**Table V.** Dihedral Angles (deg) between Planes in I and II

| atoms defining planes | I | II |
|---|---|---|
| A. N(1), N(2), N(3), N(5) | 44.5 | 52.8 |
| B. N(5), C(1), C(2), C(3), C(4), C(5) | | |
| A. N(1), N(2), N(4), N(7) | 51.7 | 51.4 |
| B. N(7), C(7), C(8), C(9), C(10), C(11) | | |

As expected, the Ru–N(isn) bond distances (weighted mean 2.099 (4) Å) were only marginally different from the Ru–$NH_3$ bond distances (weighted mean 2.125 (7) Å). The difference 0.026 (8) Å is less than that observed between $Co^{III}$–$NO_2$ and $Co^{III}$–$NH_3$ distances in the $[Co(NH_3)_5NO_2]^{2+}$ ion (difference = 0.06 Å),[12,13] where back-bonding is assumed to be absent. Thus, the principal determinants of metal–ligand bond distances in I appear to be the metal oxidation state and the nature of the $\sigma$-donor atoms. In agreement with chemical evidence, d$\pi$–$\pi^*$ interactions are not considered important in I.

The Ru–$NH_3$ bond distances may be compared to those for $[Ru(NH_3)_6](BF_4)_3$ (2.104 (4) Å),[5] $[Ru(en)_3]Cl_3{\cdot}3H_2O$ (2.11 (1) Å),[20] $[Ru_2(NH_3)_8(NH_2)_2]Cl_4$ (2.137 (3) Å),[21] and $[Ru(NH_3)_5pyz](CF_3SO_3)_3$ (2.112 (7) Å).[7] The Ru–N(isn) distances for I are also comparable to the Ru–N(pyz) distances of $[Ru(NH_3)_5pyz](CF_3SO_3)_3$ (2.076 (8) Å).[7]

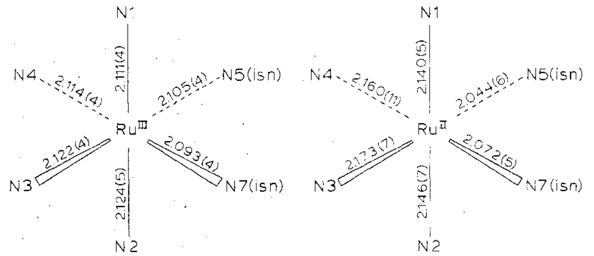

**Figure 3.** Inner coordination sphere bond distances for the cations of I (left) and II (right).

The bond angles in Table IV show that I is a slightly distorted octahedron. The source of the distortion appears purely steric in nature, with the isonicotinamides compressing the angles for $NH_3$–Ru–$NH_3$ on the opposite side of the cation.

**Structural Description of $[Ru(NH_3)_4(isn)_2](ClO_4)_2$ (II).** The atom numbering scheme for II is identical with that for I (Figure 1). The cation of II is practically superimposable on I except that the positions of O(1) and N(6) are interchanged.

The bond distances, bond angles, and dihedral angles are given in Tables III, IV, and V. Inner-sphere bond distances for I and II are shown in Figure 3.

In contrast to I, there is a significant decrease in the Ru–N(isn) compared to the Ru–$NH_3$ bond lengths. By use of the axial Ru–N distances (Ru–N(1) and Ru–N(2)), the difference is 0.083 (6) Å. In view of the preceding discussion for I and the previously noted structural[8-11] and chemical[14-17] evidence, we explain the observed differences by invoking substantial $d\pi$–$\pi^*$ interactions in the Ru–N(isn) bonds. The Ru–N(isn) distances (weighted mean 2.060 (4) Å) may be compared to those for Ru–N(py) bonds in $[(Ru(py)_4)_2C_2O_4](BF_4)_2$ (2.08 Å)[11] and the Ru–N(pyz) bond of $[Ru(NH_3)_5pyz](BF_4)_2$ (1.99 (1) Å).[7] It is noteworthy that the back-bonding in this case has a stronger effect on bond distances than increasing the charge of the ion.

The trends observed in bond angles for I are followed in II. In both I and II no abnormalities were found in bond distances and angles of the isonicotinamides.

On the basis of the data in Table III, we can state that a small trans influence is observed in II. A test based on the $\chi^2$ distribution made for the group of four Ru–$NH_3$ bond lengths indicates that the probability ($p$) that they are equal is $<0.01$. The two axial Ru–$NH_3$ distances are statistically equal and average 2.143 (5) Å, comparing almost exactly to the value of Stynes and Ibers[5] for the Ru–N distance in $[Ru(NH_3)_6]I_2$ (2.144 (4) Å). The equatorial Ru–$NH_3$ bond lengths (Ru–N(3), Ru–N(4)) are also statistically equal and average 2.170 (6) Å, for a trans bond length increase of 0.027 (8) Å. These distances may be compared to Ru–$NH_3$ bond lengths in $[(Ru(NH_3)_5)_2N_2](BF_4)_4$ (trans 2.140 (6) Å, equatorial (average) 2.12 Å),[10] $[Ru(NH_3)_5NO_2]Cl\cdot H_2O$ (trans 2.199 (6) Å, equatorial (average) 2.127 Å),[8] $[Ru(NH_3)_5Me_2SO](PF_6)_2$ (trans 2.209 (8) Å, equatorial 2.169 (5) Å),[22] $[Ru(NH_3)_5pyz](BF_4)_2$ (2.16 (1) Å),[7] and *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ (2.102 Å (average)).[9]

In view of our use of small differences in bond lengths to attribute a trans influence to the complex II, some discussion about the accuracy of the calculated structure is in order. One point to consider is the effect of excluding hydrogen atoms from the final refinement. In the present structures, inclusion of ammonia hydrogens would probably decrease all of the calculated Ru–$NH_3$ distances by approximately the same amount. It therefore appears reasonable to use the calculated bond length differences to assign a trans influence to the cation of II. It should be noted, however, that a significant distortion of the inner coordination sphere was found in structure I. In contrast to II, the Ru–$NH_3$ bond distances of I could not be statistically grouped into axial and equatorial pairs. Since distortions of a similar magnitude may be present in II, some caution should be used in considering the chemical significance of the observed trans influence.

Following the discussion of Bottomley,[9] one may take the length of the Ru–N(isn) bonds as a crude indication of the propensity of isonicotinamide to act as a $\pi$ acceptor. On this basis, acceptor capability decreases in the series: $NO^+ > NO_2^- \sim N_2 >$ isn. It is unlikely, however, that the criterion provides an ordering with respect to $\pi$-acceptor capacity without including additional provisos for the ligands chosen for comparison. The complication in ligand classification has been recognized in considering the influence of $\pi$ acceptors on the lability of ruthenium(II) complexes. Replacing ammonia with the ligands $NO^+$, $N_2$, and isn delabilizes a saturated ligand such as $H_2O$ on ruthenium(II) in decreasing order as given. In contrast, $SO_3^{2-}$, which undoubtedly has some $\pi$-acid character, is strongly labilizing, much more so than the stronger $\pi$ acid $SO_2$.[23] It is likely that $NO_2^-$ has some of the character of $SO_3^{2-}$.

Although a $\pi$ acid can be expected to weaken and thus to lengthen the bond to ruthenium(II) made by another $\pi$-acid ligand trans to it, it might well strengthen and shorten the bond to a similarly situated saturated ligand. The kinetic results cited above are consistent with such an effect though they do not require it. The structural data are inconclusive on the issue of whether $NH_3$ trans to $NO^+$ in $Ru(NH_3)_5NO^{3+}$ is at a shorter or longer distance than $NH_3$ cis to it,[9] but $NO_2^-$ does seem to exert a definite trans influence (the trans Ru–$NH_3$ distance in $[Ru(NH_3)_5NO_2]Cl$ is 0.07 Å longer than the equatorial Ru–$NH_3$ distances).[8] This bond lengthening effect is not necessarily a reflection of the $\pi$-acceptor capacity of the ligand.

The charge-transfer spectra of *cis*- and *trans*-$[Ru(NH_3)_4L_2]^{2+}$ and $[Ru(NH_3)_5L]^{2+}$ complexes, where L = isn, py, Me-isn, or pyz, have been analyzed in light of molecular orbital theory by Zwickel and Creutz.[16] They assumed that the rings of *cis*-$[RuA_4L_2]$ were oriented in the $xz$ and $yz$ planes of the octahedron. The structure of II reported here does not support that assumption. The dihedral angles formed by the plane of N(7)–isn rings with the plane of N(7), N(1), N(2), and N(4) is 51.4°. The related angle for N(5)–isn and N(5), N(2), N(3), and N(1) is 52.8°. This result does not invalidate the arguments of Zwickel and Creutz, however. Appropriate linear combinations of the Ru(II) basis orbitals can be chosen to yield the same results.

In the context of data of the kind we have obtained, those obtained for the mixed-valence ion $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ came up for consideration.[24] For this species, Ru–$NH_3$ distances are reported as 2.116 Å (av) and Ru–N(pyz) distances as 2.006 (6) Å. However, in view of the substantial difference in the $Ru^{II}$–N (heterocyclic) distance for II (2.060 (4) Å) and that for $[Ru(NH_3)_5pyz]^{2+}$ (1.99 (1) Å), we feel that our observations do not help to clarify the interesting questions about the electronic structure of the mixed-valence ion.

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**Registry No.** I, 70368-87-5; II, 31279-73-9.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes and root mean square amplitudes of thermal vibration for $[Ru(NH_3)_4(isn)_2](ClO_4)_3\cdot H_2O$ and $[Ru(NH_3)_4(isn)_2](ClO_4)_2$ (26 pages). Ordering information is given on any current masthead page.

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# Crystal and Molecular Structure of Two Crystalline Modifications of Bis[1-methyl-3-(2-chloro-6-methylphenyl)triazine 1-oxidato]nickel(II), NiBPT—a Bis Chelate with a Five-Membered Ni–N–O Ring

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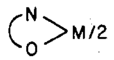
The title compound is obtained in two different crystalline modifications. The green elongated parallelepiped crystals obtained from acetone solutions belong to the monoclinic space group $P2_1/a$ with $Z = 4$, $a = 14.306$ (3) Å, $b = 7.858$ (1) Å, $c = 18.605$ (3) Å, $\beta = 103.72$ (3)°, $d_{\text{calcd}} = 1.489$ g/cm$^3$, and $d_{\text{measd}} = 1.50$ g/cm$^3$. A benzene solvate, NiBPT·$C_6H_6$, belonging to the space group $P\bar{1}$ is obtained from benzene solutions and has $Z = 1$, $a = 7.9637$ (9) Å, $b = 9.246$ (2) Å, $c = 9.999$ (2) Å, $\alpha = 63.93$ (1)°, $\beta = 77.44$ (1)°, $\gamma = 68.57$ (1)°, $d_{\text{calcd}} = 1.442$ g/cm$^3$, and $d_{\text{measd}} = 1.42$ g/cm$^3$. The structures of both crystals were determined by using three-dimensional diffractometer data. In the case of NiBPT, full-matrix least-squares refinement using 2731 reflections having $I > 2\sigma(I)$ led to a conventional $R$ value of 0.071. For NiBPT·$C_6H_6$ the refinement using 1523 reflections having $I > 3\sigma(I)$ converged to an $R$ value of 0.032. The coordination in the $NiN_2O_2$ moiety is strictly planar in both modifications with Ni–O and Ni–N distances of 1.849 (4) and 1.846 (6) Å, respectively, and a N–Ni–O angle of 83.4 (2)°. (The values are averaged over the two structure determinations. The root-mean-square value of the esd's in individual measurements is given in parentheses.) The benzene molecule in the solvated crystal is situated too far from the nickel atom to have any appreciable interaction with it. The analogous cobalt complex, CoBPT, is shown to be isomorphous with NiBPT.

## Introduction

Aromatic triazine 1-oxides, having the general formula Ar—NH—N=N(R)→O, where Ar is a phenyl or substituted phenyl group and R is an alkyl or aryl group, are potentially bidentate ligands which are known to form both bis and tris chelate complexes with various metal ions.[3] The coordination geometry and magnetic properties of the bis chelates are extremely sensitive to the number and nature of the substituents on the aromatic ring. Unsubstituted and methyl-substituted complexes of cobalt, for example, are not stable in air and could not be isolated.[3a] When Ar is $o$-$C_6H_4X$, where X = F, Cl, Br, $OCH_3$, $OC_2H_5$, or $SCH_3$, the ligand forms pseudooctahedral complexes involving a weak coordination of the halo group, while the iodo-substituted complex appears to be planar ($\mu_{\text{eff}} = 2.1\ \mu_B$) in the solid state and pseudooctahedral in solution ($\mu_{\text{eff}} = 4.4\ \mu_B$ in benzene solution).[3e] Disubstituted ligands with substituents at 2- and 6-positions form predominantly planar complexes.[3f] We had chosen one such complex, viz., CoBPT, for investigation as part of our more general project on the electronic structure of low-spin cobalt(II) complexes. In the course of our electron paramagnetic resonance (EPR) studies on this complex, it was felt that the interpretation of the single-crystal spectra and the analysis of the magnetic parameters would be greatly facilitated by a knowledge of the crystal structure of the corresponding isomorphous nickel complex, which was used as the host lattice for EPR measurements. In addition, we were interested in verifying an earlier hypothesis[4] regarding the weak coordination of the chlorine atom, which was suggested to be responsible for the large electric field gradient at the cobalt nucleus which manifested itself as a large quadrupole term in the spin Hamiltonian. In fact, such a weak chloro coordination had been established by crystal structure determination[5] in a similar cobalt complex, bis[1-methyl-3-($o$-chlorophenyl)triazine 1-oxidato]cobalt(II) (CoBPTH).

Even though the crystal structure investigation was taken up with the above-mentioned objectives in mind, we found in the course of our work that the structure of the nickel complex is interesting in its own right. While the literature on the structure and stereochemistry of bis chelate complexes of the type



is quite prolific, they are mostly confined to systems with six-membered chelate rings.[6] Detailed structural data on five-membered ring complexes are limited to a few copper complexes,[7] even though a large number of such complexes have been characterized by other methods.[6] Hence the present structural report is believed to be of general interest in relation to the stereochemistry of bis chelate metal complexes.

NiBPT crystallizes in two crystalline modifications. A monoclinic form is obtained from most solvents such as chloroform, acetone, etc., while a triclinic modification results from benzene solutions. The latter modification turned out to be a benzene solvate containing weakly bound benzene in the lattice. These crystals rapidly lose benzene on standing and become powdery. A thermogravimetric analysis showed a weight loss corresponding to 1 mol of benzene. The crystal structures of both types of crystals are discussed in this report.

## Experimental Section

**Bis[1-methyl-3-(2-chloro-6-methylphenyl)triazine 1-oxidato]nickel(II)** was prepared as previously reported.[3d,f] Crystals of NiBPT suitable for X-ray work were obtained in the form of elongated parallelepipeds by slow evaporation of an acetone solution. Single crystals of NiBPT·$C_6H_6$ were obtained by slow evaporation of a

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