significantly greater than that of other similar complexes (Table V). We feel that the extra lengthening is due, primarily, to increased ligand size, which results in a weaker Ni–P apical bond.

Further support for the weak nature of apical ligand bonding comes from ^{31}P NMR studies. Preliminary qualitative ^{31}P NMR data on our complexes show that for **1** in C_6D_6 the spectrum at room temperature shows two peaks at 29.9 and 1.8 ppm. These have been assigned to **1** and **2**, respectively. The ratio of the two peaks indicates that about 7% of **2** is present at 21 °C. Heating the sample at 70 °C for 15 min affords a sample in which **1** and **2** are present in about equal amounts. Further heating for 1 h affords **2** almost exclusively.

The dissociation of pentacoordinated nickel(II)–phosphine complexes is well-known. However, pentacoordinated nickel complexes of the formula $[Ni(CN)_2P_3]$ are, in general, quite stable to dissociation.[17] This stability has been attributed to the presence of the cyano group in the complex. For example, it was not possible to isolate square-planar complexes of the type $[Ni(CN)_2P_2]$ where P = PMe_2Ph, $PMePh_2$ or $P(C_6F_5)Me_2$; only the 5-coordinate species $[Ni(CN)_2P_3]$ could be obtained.[17] Also, the ^{31}P NMR spectrum of $[Ni(CN)_2P_3]$ showed the presence of only a small quantity of $[Ni(CN)_2(PMe_3)_2]$ in solution.[19] The dissociation of **1** is then quite remarkable and is similar in magnitude to the dissociaton of $[Ni(CN)_2(PEtPh_2)_3]$ (ca. 20%).[17] The ligand $PEtPh_2$ is very similar in size to $P(CH_2OH)Ph_2$, and the amount of dissociation indicates that the apical Ni–P distance in $[Ni(CN)_2(PEtPh_2)_3]$ should be of similar length to that found in **1**. In conclusion, both our ^{31}P NMR and X-ray data indicate that steric effects play a significant role in determining the stability of 5-coordinated nickel(II) complexes to dissociation. Our results are in agreement with those of Meek[17] on $[Ni(CN)_2(PEtPh_2)_3]$ and related complexes, which show that electronic arguments alone are unable to account for the spectroscopic and structural findings.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Committee on Research for the University of California, and the Research Corp. for the support of this research and Shaun Wilson for experimental assistance.

Registry No. **1**, 88158-03-6; **2**, 88179-93-5; $Na_2[Ni(CN)_4]$, 14038-85-8; $P(CH_2OH)Ph_2$, 5958-44-1; diphenylphosphine, 829-85-6; formaldehyde, 50-00-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes in addition to complete tables of bond distances, angles, and thermal parameters (24 pages). Ordering information is given on any current masthead page.

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Preparation, Spectra, and Crystal Structures of Two Rhodium(III) Complexes with Short Intramolecular Hydrogen Bonds

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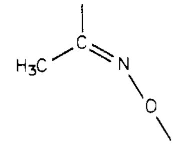
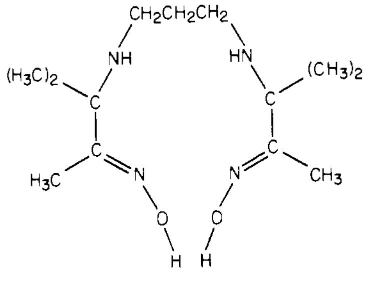
In the reactions of the tetradentate ligand 3,3′-(1,3-propanediyldiimino)bis(3-methyl-2-butanone oxime) (PnAO) and the bidentate ligand 3-amino-3-methyl-2-butanone oxime (AO) with $RhCl_3$ in aqueous ethanol, the neutral *trans*-dichloro complexes $[Rh(PnAO\text{-}H)Cl_2]$ and $[Rh((AO)_2\text{-}H)Cl_2]$, respectively, are formed with the elimination of one hydrogen ion from an oxime group. The resulting complexes have a strong hydrogen bond between cis oxime groups (O---O = 2.474 (7) and 2.459 (2) Å, respectively). This hydrogen bond can be seen as a broad band in the IR spectra at 1792 and 1785 cm^{-1} and in proton chemical shifts of 18.9 and 19.3 ppm downfield from Me_4Si, respectively. The average Rh–ligand distances are Rh–Cl = 2.336 (10) Å, Rh–N(oxime) = 1.988 (2) Å, and Rh–N(amine) = 2.064 (8) Å. $[Rh(PnAO\text{-}H)Cl_2]$ crystallizes in the orthorhombic space group $P2_12_12_1$: a = 8.400 (2) Å, b = 13.149 Å (5) Å, c = 16.065 (3) Å, Z = 4, d_{calcd} = 1.668 (1) g/cm^3. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final R value of 0.043 for the 2579 reflections with $I > 2\sigma(I)$. $[Rh((AO)_2\text{-}H)Cl_2]$ crystallizes in the orthohombic space group *Pnam*: a = 11.108 (1) Å, b = 11.993 (1) Å, c = 11.661 (2) Å, Z = 4, d_{obsd} = 1.732 (1) g/cm^3. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final R value of 0.020 for the 2609 reflections with $I > 2\sigma(I)$. This complex has a mirror plane containing the rhodium, two chlorines, and the hydrogen-bonded hydrogen atom.

Introduction

Cobalt(III) complexes of the ligands AO and PnAO have been previously reported,[1] and the crystal structures of $[Co((AO)_2\text{-}H)Cl_2]$[2] and of $[Co(PnAO\text{-}H)(NO_2)_2]$[3] have revealed the presence of very strong intramolecular hydrogen bonds (O---O = 2.422 (3) and 2.432 (3) Å, respectively). The purpose of this study was to examine the effect of the larger Rh(III) atom on the hydrogen bond with and without the steric constraint of the propylene bridge between the amine nitrogen atoms. At least in the case of the PnAO complex, some lengthening of the O---O distance might be expected on steric grounds.



AO



PnAO

Experimental Section

Synthesis. Ligands. The ligands 3,3′-(1,3-propanediyldiimino)-

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(1) Murmann, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 521–526.

(2) Schlemper, E. O.; Laplaca, S. J.; Davis, B. R.; Hamilton, W. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 918–920.

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0020-1669/84/1323-0330$01.50/0

Table I. Crystal Data, Data Collection Parameters, and Refinement Results for [Rh(PnAO-H)Cl_2] and [Rh($(AO)_2$-H)Cl_2]

	[Rh(PnAO-H)Cl_2]	[Rh($(AO)_2$-H)Cl_2]
formula	$RhCl_2O_2N_4C_{13}H_{27}$	$RhCl_2O_2N_4C_{10}H_{23}$
cryst type (dimens, mm)	distorted octahedron (0.37 × 0.23 × 0.17)	prism (0.30 × 0.17 × 0.10)
fw	445.2	405.1
d_{calcd}, g/cm^3	1.668 (2)	1.732 (1)
d_{obsd}(flotation), g/cm^3	1.66 (1)	1.73 (1)
space group	$P2_12_12_1$	*Pnam*
a, Å	8.400 (2)	11.108 (1)
b, Å	13.149 (5)	11.993 (2)
c, Å	16.065 (3)	11.661 (2)
Z	4	4
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromation	graphite crystal	graphite crystal
scan technique	θ–2θ step (16 bkgd, 64 pk, 16 bkgd)	θ–2θ step (16 bkgd, 64 pk, 16 bkgd)
scan width, deg	$1.10 + 0.35 \tan \theta$	$0.70 + 0.35 \tan \theta$
scan time	to obtain 3% counting statistics to a max of 120 s	same (max 90 s)
no. of reflcns measd	3473	4654
max 2θ, deg	50	60
reflcn classes	hkl and $\bar{h}\bar{k}\bar{l}$	hkl and $\bar{h}\bar{k}\bar{l}$ (~$^2/_3$ of range)
no. of unique reflcns	3116	2855
no. of reflcns >2σ used in refinement	2579	2609
μ, cm^{-1}	12.6	14.8
transmissn range for empirical abs cor	0.93–1.00	0.88–1.00
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma F_o$	0.043	0.020
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w F_o{}^2)^{1/2}$	0.048	0.035
error in observn of unit weight	1.23	1.28

bis(3-methyl-2-butanone oxime) (hereafter PnAO) and 3-amino-3-methyl-2-butanone oxime (hereafter AO) were prepared as described by Murmann.[1,4]

[Rh(PnAO-H)Cl_2]. To an aqueous solution containing hydrated rhodium trichloride (2.2 mmol in 5 mL of water) was added an ethanolic solution of PnAO (2.3 mmol in 10 mL of ethanol). The red mixture was heated under reflux for about 3 h to produce a yellow-orange solution. From this, a black suspended solid was removed by filtration. The volume was reduced, by standing, to about half over a period of 1 week. When 3.2 mL of 0.98 M KOH (3.1 mmol) was added with stirring, a yellow precipitate was formed in about 40% yield. This product was collected, washed with a small amount of water, and dried in a desiccator over anhydrous $CaCl_2$. The compound is very insoluble in water and only slightly soluble in acetone, ethanol, and Me_2SO. Yellow, octahedral-shaped crystals were obtained by recrystallization from Me_2SO. Anal. Calcd for $RhC_{13}H_{25}N_4O_2Cl_2$: C, 35.23; H, 5.69; N, 12.64; Cl, 16.00. Found: C, 35.23; H, 6.04; N, 12.58; Cl, 16.10.

[Rh($(AO)_2$-H)Cl_2]. To an aqueous solution of hydrated rhodium trichloride (1.4 mmol in 5 mL of water) was added an ethanolic solution of AO·HCl (3.1 mmol in 15 mL of ethanol). To this red mixture was added 3.4 mmol of solid KOH. The slurry was heated under reflux for 0.5 h until it became clear and yellow-orange. The mixture was filtered hot and yielded well-formed, yellow-orange crystals on cooling to room temperature (isolated yield ~23%). The complex can be recrystallized from ethanol–water mixtures. Anal. Calcd for $RhCl_2O_2H_4C_{10}H_{23}$: C, 29.65; H, 5.72; N, 13.83; Cl, 17.50. Found: C, 29.59; H, 5.77; N, 13.85; Cl, 17.67.

NMR Spectra. The spectra were recorded on a Varian EM-360 spectrometer with tetramethylsilane (Me_4Si) as an internal standard in dimethyl-d_6 sulfoxide.

Infrared Spectra. Solid-state infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer using Fluorolube mulls.

Collection and Reduction of X-ray Data. Diffraction data were collected at 22 (1) °C on an Enraf-Nonius CAD4 automated diffractometer using Mo Kα radiation (λ = 0.7107 Å). Lattice constants were obtained by least-squares fit of 25 carefully centered reflections on each compound. The intensities of three standard reflections measured after each 8000 s of X-ray exposure showed no significant variation. Orientation was checked after every 200 reflections by using three orientation standards, and reorientation by recentering 25 reflections was done if any of the three were significantly off-center. A summary of cell data, data collection parameters, and refinement results is included in Table I. All calculations were done on a PDP11/34 computer using the Nonius SDP programs.

Table II. Positional Parameters for [Rh($(AO)_2$-H)Cl_2][a]

atom	x	y	z
Rh	0.220 87 (1)	−0.181 01 (1)	0.2500
Cl(1)	0.128 23 (5)	−0.006 80 (4)	0.2500
Cl(2)	0.316 12 (5)	−0.355 47 (4)	0.2500
O(1)	0.432 38 (9)	−0.082 85 (9)	0.14454 (9)
N(1)	0.325 35 (9)	−0.131 61 (9)	0.1210 (1)
N(2)	0.111 56 (10)	−0.223 10 (11)	0.1127 (1)
C(1)	0.288 9 (1)	−0.141 1 (1)	0.0176 (1)
C(2)	0.171 0 (1)	−0.203 4 (1)	−0.0011 (1)
C(3)	0.357 7 (2)	−0.097 8 (1)	−0.0823 (1)
C(4)	0.199 7 (2)	−0.316 1 (1)	−0.0549 (2)
C(5)	0.086 0 (2)	−0.134 3 (2)	−0.0753 (2)

[a] Standard deviations from the full-matrix least-squares refinement are given in parentheses here and elsewhere in the paper.

Solution and Refinement of the Structures. Both structures were solved by conventional Patterson and Fourier methods. In the case of [Rh($(AO)_2$-H)Cl_2] only half of the molecule is symmetry independent with the mirror passing through the rhodium, two chlorines, and the center of the short hydrogen bond. The full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$, $\sigma(F_o) = \sigma(F_o{}^2)/2F_o$, $\sigma^2(F_o{}^2) = \sigma^2{}_{counting} + (pF_o{}^2)^2$, and p = 0.050 for the PnAO complex and 0.045 for the AO complex. Atomic scattering factors were taken from ref 5 and included anomalous scattering contributions. For the PnAO complex the hydrogen atoms were placed in fixed positions on the basis of difference Fourier syntheses and chemical reasonability (the hydrogen position for the hydrogen bond was refined). For the AO complex the hydrogen positions were refined (B fixed at 5 Å^2). For the PnAO complex the maximum residual was about 0.6 e/Å^3 in the vicinity of the rhodium atom while for the AO complex that residual was only about 0.5 e/Å^3.

The final positional parameters for the non-hydrogen atoms are included in Tables II and III for the AO and the PnAO complexes, respectively. Parameters for hydrogen atoms, thermal parameters, and listings of observed and calculated structure factors are available as supplementary material.

Results and Discussion

Both complexes are discrete, mononuclear, neutral rhodium(III) molecules with nearly octahedral coordination of the rhodium (PnAO complex in Figure 1 and AO complex in Figure 2). The octahedron about the rhodium is completed

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(4) (a) Murmann, R. K. *J. Am. Chem. Soc.* **1958**, *80*, 4174–4180. (b) Vassian, E. G.; Murmann, R. K. *Inorg. Chem.* **1967**, *6*, 2043–2046.

(5) "International Tables for X-ray Crystallography"; Kynoch Press: Brimingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

Table III. Positional Parameters for [Rh(PnAO-H)Cl_2]

atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh	0.03670 (6)	0.04632 (4)	0.13582 (3)	1.820 (7)
Cl(1)	−0.1197 (2)	0.0285 (2)	0.2385 (1)	2.83 (4)
Cl(2)	0.1898 (2)	0.1247 (2)	0.0322 (1)	3.51 (4)
O(1)	0.0834 (6)	−0.1471 (4)	0.0547 (3)	3.3 (1)
O(2)	0.2827 (6)	−0.1030 (4)	0.1622 (3)	3.1 (1)
N(1)	−0.0157 (6)	−0.0669 (4)	0.0585 (3)	2.0 (1)
N(2)	0.2296 (7)	−0.0127 (5)	0.1887 (4)	2.4 (1)
N(3)	−0.1617 (7)	0.1070 (5)	0.0783 (4)	2.8 (1)
N(4)	0.0966 (7)	0.1641 (5)	0.2138 (4)	3.0 (1)
C(1)	−0.1441 (8)	−0.0622 (6)	0.0149 (4)	2.6 (2)
C(2)	0.2975 (8)	0.0344 (6)	0.2488 (4)	2.4 (1)
C(3)	−0.2492 (9)	0.0298 (6)	0.0264 (4)	2.8 (2)
C(4)	0.2257 (9)	0.1357 (6)	0.2760 (5)	3.0 (2)
C(5)	−0.192 (1)	−0.1442 (8)	−0.0432 (6)	4.0 (2)
C(6)	0.437 (1)	−0.0086 (7)	0.2933 (5)	4.0 (2)
C(7)	−0.402 (1)	−0.0057 (8)	0.0707 (6)	4.3 (2)
C(8)	−0.288 (1)	0.0792 (9)	−0.0560 (6)	5.4 (3)
C(9)	0.156 (1)	0.1249 (8)	0.3634 (6)	5.2 (2)
C(10)	0.352 (1)	0.2188 (7)	0.2720 (8)	5.3 (3)
C(11)	−0.2511 (9)	0.1794 (6)	0.1305 (6)	3.3 (2)
C(12)	−0.150 (1)	0.2572 (6)	0.1734 (5)	3.4 (2)
C(13)	−0.040 (1)	0.2226 (6)	0.2429 (5)	3.6 (2)
HOO	0.24 (1)	−0.125 (7)	0.117 (5)	

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

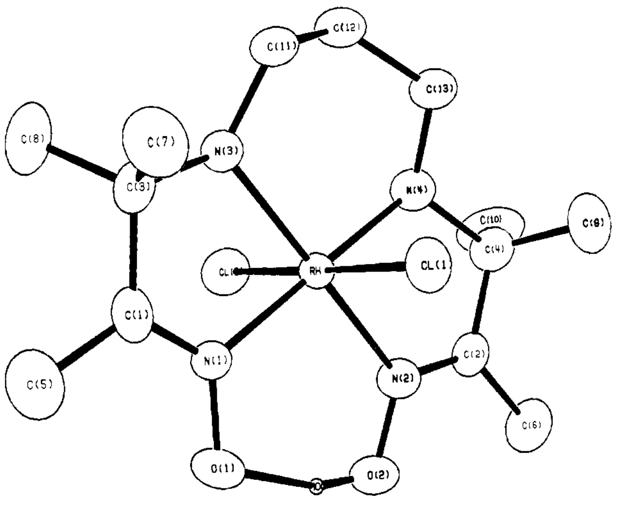

Figure 1. Perspective view of the [Rh(PnAO-H)Cl_2] molecule showing the atom labeling and thermal ellipsoids (50% probability).

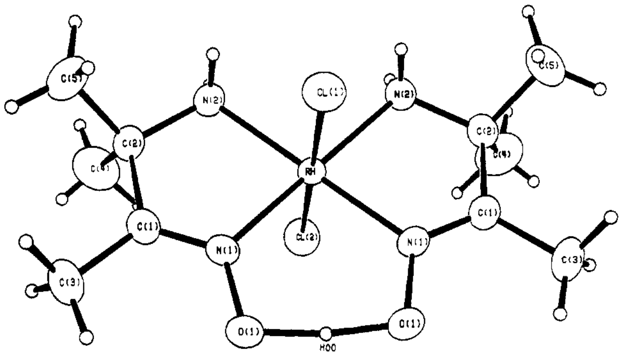

Figure 2. Perspective view of the [Rh($(AO)_2$-H)Cl_2] molecule showing the atom labeling and thermal ellipsoids (50% probability).

by the two cis oxime nitrogens, the two cis amine nitrogens, and two chloro ligands in trans position. Both complexes have essentially the same O---O distance for the short hydrogen bond.

A stereoscopic view of the unit cell contents of the PnAO complex is given in Figure 3 (supplementary material). Intermolecular contacts, as given in Table IV (supplementary material), indicate only van der Waals interactions. There is no intermolecular hydrogen bonding. A least-squares plane through the rhodium and the four coordinated nitrogens show that the rhodium is 0.021 (2) Å out of the nitrogen plane toward Cl(1). That chlorine has a shorter bond to rhodium (2.327 (2) Å) than does the other chlorine (2.343 (2) Å). The latter chlorine (Cl(2)) is apparently weakly hydrogen bonded to both HN3 and HN4 (Cl(2)–N(3) = 3.053 (7) Å, Cl(2)–HN3 = 2.72 Å, Cl(2)–HN3–N(3) = 103°, Cl(2)–N(4) = 3.064 (7) Å, Cl(2)–HN4 = 2.71 Å, Cl(2)–HN4–N(4) = 105°). The six-membered ring involving the propylene bridge is in the chair configuration. Methyl carbon atoms C(7) and C(9) are nearly perpendicular to the coordination plane (1.66 (1) and 1.60 (1) Å, respectively, from the plane) while C(8) and C(10) are on the other side of the plane by 0.79 (1) and 0.90 (1) Å, respectively. For the PnAO complex the important intramolecular bond lengths and bond angles are in Table V.

Table V. Bond Distances (Å) and Angles (deg) for [Rh(PnAO-H)Cl_2]

		Distances			
Rh–Cl(1)	2.327 (2)	O(2)–HOO	0.86 (9)	C(2)–C(4)	1.526 (10)
Rh–Cl(2)	2.343 (2)	N(1)–C(1)	1.288 (8)	C(2)–C(6)	1.485 (10)
Rh–N(1)	1.988 (5)	N(2)–C(2)	1.281 (9)	C(3)–C(7)	1.541 (11)
Rh–N(2)	1.987 (6)	N(3)–C(3)	1.505 (9)	C(3)–C(8)	1.511 (11)
Rh–N(3)	2.066 (6)	N(3)–C(11)	1.474 (9)	C(4)–C(9)	1.528 (12)
Rh–N(4)	2.055 (6)	N(4)–C(4)	1.521 (9)	C(4)–C(10)	1.523 (11)
O(1)–N(1)	1.344 (7)	N(4)–C(13)	1.457 (10)	C(11)–C(12)	1.498 (11)
O(1)–HOO	1.67 (9)	C(1)–C(3)	1.509 (11)	C(12)–C(13)	1.519 (11)
O(2)–N(2)	1.338 (8)	C(1)–C(5)	1.483 (11)	O(1)–O(2)	2.474 (7)
		Angles			
Cl(1)–Rh–Cl(2)	178.65 (8)	N(1)–O(1)–HOO	109 (4)	C(1)–C(3)–C(7)	107.6 (6)
Cl(1)–Rh–N(1)	90.1 (2)	N(2)–O(2)–HOO	115 (7)	C(1)–C(3)–C(8)	111.3 (7)
Cl(1)–Rh–N(2)	89.6 (2)	O(1)–N(1)–C(1)	122.1 (6)	C(7)–C(3)–C(8)	110.8 (7)
Cl(1)–Rh–N(3)	91.4 (2)	O(2)–N(2)–C(2)	121.4 (6)	N(4)–C(4)–C(2)	107.9 (6)
Cl(2)–Rh–N(1)	90.4 (2)	C(4)–N(4)–C(13)	118.7 (6)	N(4)–C(4)–C(10)	106.9 (7)
Cl(2)–Rh–N(2)	91.6 (2)	N(1)–C(1)–C(3)	117.5 (6)	C(2)–C(4)–C(9)	109.4 (7)
Cl(2)–Rh–N(3)	87.4 (2)	N(1)–C(1)–C(5)	122.5 (7)	C(2)–C(4)–C(10)	109.9 (6)
Cl(2)–Rh–N(4)	88.1 (2)	C(3)–C(1)–C(5)	120.0 (6)	C(9)–C(4)–C(10)	111.9 (8)
N(1)–Rh–N(2)	98.9 (2)	N(2)–C(2)–C(4)	117.5 (6)	N(3)–C(11)–C(12)	114.4 (6)
N(1)–Rh–N(3)	80.3 (2)	N(2)–C(2)–C(6)	122.0 (7)	C(11)–C(12)–C(13)	118.6 (7)
N(1)–Rh–N(4)	178.4 (2)	C(4)–C(2)–C(6)	120.4 (6)	N(4)–C(13)–C(12)	113.7 (6)
N(2)–Rh–N(3)	178.8 (3)	N(3)–C(3)–C(1)	108.9 (5)	O(1)–HOO–O(2)	154
N(2)–Rh–N(4)	80.4 (3)	N(3)–C(3)–C(7)	110.9 (6)		
N(3)–Rh–N(4)	100.3 (3)	N(3)–C(3)–C(8)	107.5 (7)		

Table VI. Bond Distances (Å) and Bond Angles (deg) for $[Rh((AO)_2\text{-}H)Cl]$

		Distances			
Rh–Cl(1)	2.329 (1)	O(1)–HOO	1.233 (3)	C(1)–C(2)	1.523 (2)
Rh–Cl(2)	2.345 (1)	O(1)–O(1)	2.459 (2)	C(1)–C(3)	1.487 (2)
Rh–N(1)	1.990 (1)	N(1)–C(1)	1.277 (2)	C(2)–C(4)	1.524 (2)
Rh–N(2)	2.072 (1)	N(2)–C(2)	1.501 (2)	C(2)–C(5)	1.526 (2)
N(1)–O(1)	1.353 (1)				
		Angles			
Cl(1)–Rh–Cl(2)	179.40 (2)	N(2)–Rh–N(2)	101.21 (4)	N(2)–C(2)–C(4)	108.5 (1)
Cl(1)–Rh–N(1)	89.46 (3)	N(1)–C(1)–C(2)	116.8 (1)	N(2)–C(2)–C(5)	108.3 (1)
Cl(1)–Rh–N(2)	87.69 (4)	N(1)–C(1)–C(3)	123.1 (1)	N(2)–C(2)–C(1)	109.2 (1)
Cl(2)–Rh–N(1)	90.15 (3)	C(2)–C(1)–C(3)	120.0 (1)	C(1)–C(2)–C(4)	108.3 (1)
Cl(2)–Rh–N(2)	92.69 (4)	O(1)–N(1)–C(1)	120.6 (1)	C(1)–C(2)–C(5)	110.3 (1)
N(1)–Rh–N(1)	98.20 (4)	O(1)–N(1)–Rh	119.20 (8)	C(4)–C(2)–C(5)	112.2 (2)
N(1)–Rh–N(2)	80.23 (4)	C(1)–N(1)–Rh	120.16 (8)	O(1)–HOO–O(1)	172 (2)
N(1)–Rh–N(2)	176.74 (4)	C(2)–N(2)–Rh	112.75 (8)		

Table VII. Comparison of Average Bond Distances (Å) and Angles (deg)

compd	O---O	M–N(oxime)	M–N(amine)	N(oxime)–M–N(amine)	N(oxime)–M–N(oxime)	N(amine)–M–N(amine)	diffraction method	ref
$[Co((AO)_2\text{-}H)Cl_2]$	2.422 (3)	1.891 (2)	1.947 (2)	82.53 (8)	99.0 (1)	95.8 (1)	X-ray	2
$[Co(PnAO\text{-}H)(NO_2)_2]$	2.432 (3)	1.900 (3)	1.977 (3)	82.1 (1)	98.6 (1)	97.1 (1)	X-ray	3
$[Ni((AO)_2\text{-}H)]Cl\cdot H_2O$	2.420 (3)	1.866 (1)	1.908 (1)	83.07 (6)	97.34 (6)	96.53 (6)	neutron	6
$[Ni(PnAO\text{-}H)]Cl\cdot H_2O$	2.41 (1)	1.884 (5)	1.937 (5)	83.02 (2)	95.9 (2)	97.7 (2)	neutron	8
$[Pd(PnAO\text{-}H)]NO_3$	2.474 (5)	1.969 (4)	2.040 (4)	80.6 (2)	97.4 (2)	101.5 (2)	X-ray	9
$[Pt((AO)_2\text{-}H)]Cl\cdot 3.5H_2O$	2.472 (5)	1.986 (2)	2.054 (6)	79.60 (2)	97.5 (1)	103.3 (1)	neutron	7
$[Rh((AO)_2\text{-}H)Cl_2]$	2.459 (2)	1.990 (1)	2.072 (1)	80.23 (4)	98.2 (4)	101.2 (4)	X-ray	this work
$[Rh(PnAO\text{-}H)Cl_2]$	2.474 (7)	1.987 (5)	2.060 (6)	80.3 (3)	98.9 (2)	100.3 (3)	X-ray	this work

Although the errors are rather large due to the limited accuracy of the data set, the average values of chemically equivalent bond distances are normal. Individual values are in general within 1 or 2 standard deviations of the average value.

In contrast, an excellent data set for the AO complex was obtained, and this is reflected in the increased precision of the results. Bond distances and bond angles are in Table VI. Since only half the molecule is symmetry independent, chemically equivalent distances are also symmetry equivalent. Thus, the comparison made above for the PnAO complex is not possible. The bond distances are however in good agreement with corresponding average values for the PnAO complex. The hydrogen atom in the short O---O hydrogen bond (2.459 (2) Å) is fixed by symmetry to be perfectly centered. The compound is isomorphous with the corresponding cobalt complex,[2] which exhibits very similar intraligand distances. In addition, the chelate rings are nearly planar as in the cobalt complex, which contrasts with the puckering observed for the square-planar Ni(II) complex of the same ligand. Only a slight lengthening of the O---O hydrogen bond occurs in this complex compared with the cobalt complex[2] (O---O = 2.422 (3) Å) despite the increase in M–N distances (Co–N(amine) = 1.891 (2), Rh–N(amine) = 1.990 (1), Co–N(oxime) = 1.947 (2), Rh–N(oxime) = 2.072 (1) Å). A nearly identical O---O distance is maintained by an opening of the N(amine)–Rh–N(amine) angle (101.2 (1)°), compared with 95.8 (1)° in the cobalt complex. A similar effect was observed in comparison of the square-planar Ni(II)[6] (96.53 (6)°) and Pt(II)[7] (103.3 (1)°) complexes where again only a modest increase in O---O distance from 2.420 (3) to 2.472 (5) Å was observed.

There are no unusual intermolecular contacts (the crystal packing can be seen in Figure 4 (supplementary material)). In $[Rh((AO)_2\text{-}H)Cl_2]$ the shortest intermolecular contact is between the oxime oxygen and an amine nitrogen (O(1)---N(2) = 3.085 (2) Å, N(2)–H1N2---O(1) = 153 (1)°, H1N2---O(1) = 2.27 (2) Å), which is a weak hydrogen bond. There is also a weak intramolecular hydrogen bond between Cl(1) and N(2) with Cl(1)–N(2) = 3.054 (1) Å, H2N2---Cl(1) = 2.64 (2) Å, and Cl(1)---HN2–N(2) = 109 (2)°. This may be correlated with the longer (by 0.016 Å) Rh–Cl(1) distance compared with the Rh–Cl(2) distance.

As in the Ni(II), Pt(II), and Pd(II) complexes,[6–9] the average Rh–N(amine) bond distances in this study (see Table VII) are significantly longer than the average Rh–N(oxime) bond distances. Because of the increased size of the metal, the metal–nitrogen bond lengths in the Rh(III) complexes are longer than those in the Co(III) complexes with the corresponding ligand.[2,3] All the C–C and C–N distances in the ligand are quite normal and agree within experimental error with the corresponding distances observed in other α-amine oxime complexes[2–9] of Co(III), Ni(II), Pt(II), and Pd(II).

The N(amine)–M–N(amine), N(amine)–M–N(oxime), and N(oxime)–M–N(oxime) angles in the PnAO complex of Rh(III) are very close to the corresponding angles in the AO complex (see Table VII). A similar observation was also found in the AO and PnAO complexes of Co(III).[2,3] The N(amine)–M–N(amine) angles of Rh(III) complexes in this study are larger than those in Co(III) complexes with the corresponding ligand. In contrast, the N(amine)–M–N(oxime) angles of Rh(III) complexes are smaller than those in the corresponding Co(III) complexes. This is because of the different size of Co(III) and Rh(III) ions. Similar observations were also found for $[Ni((AO)_2\text{-}H)]Cl\cdot H_2O$[5,6] compared with $[Pt((AO)_2\text{-}H)]Cl\cdot H_2O$[7] and for $[Ni(PnAO\text{-}H)]Cl\cdot H_2O$[8] compared with $[Pd(PnAO\text{-}H)]\cdot NO_3$.[9] The N(amine)–M–N(amine) angles of Rh(III) complexes of AO and PnAO are larger than the N(oxime)–M–N(oxime) angles, in contrast to the Co(III) complexes of the corresponding ligand where N(amine)–M–N(amine) angles are invariably smaller than the N(oxime)–M–N(oxime) angles. Since the angles are consistent for a particular metal, the steric requirements of the PnAO ligand are almost the same as those of two AO

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ligands, and the propylene bridge in PnAO complexes imposes no significant constraint on these complexes.

An X-ray diffraction study of [Co((AO)$_2$-H)Cl$_2$][2] has revealed an O---O distance of 2.422 (3) Å. With that same bidentate α-amine oxime ligand occupying a square plane in [Rh((AO)$_2$-H)Cl$_2$], an O---O distance of 2.459 (2) Å is observed. In [Rh(PnAO-H)Cl$_2$], the O---O distance is 2.474 (7) Å, which is longer than 2.432 (3) Å observed in the [Co(PnAO-H)(NO$_2$)$_2$] complex.[3] The above results reveal the effect of the size of the metal ion on the hydrogen bond. The elongation of 0.037–0.042 Å in the O---O distance on going from Co(III) to Rh(III) can be associated with the larger size of Rh(III). The increase in the M–N–O angle by about 2° on going from Rh to Co further indicates the different effects of the two metals and suggests a repulsive interaction of the oxygen atoms in the cobalt complexes. In nickel(II) complexes,[6,8] this angle is also approximately 2° larger than in the corresponding Pd(II)[9] and Pt(II)[7] complexes.

The infrared spectra have no unusual features except the broad band at 1785 (5) cm^{-1} for each compound that is associated with the short O---H---O hydrogen bond.

The proton NMR spectrum of [Rh(PnAO-H)Cl$_2$] has methyl proton resonances (2:1 ratio) at 1.40 and 2.05 ppm relative to Me$_4$Si. The former is a bit broader, which is attributed to the slight difference in environment of the two methyl groups on a chelate-ring sp^3 carbon (C(7) and C(9) compared with C(8) and C(10)). The methylene protons are apparently strongly coupled and result in a broad multiplet at 3.05 ppm while the amine hydrogens give a broad resonance at 4.80 ppm. The O--H---O hydrogen-bond resonance appears at 18.9 ppm. For [Rh((AO)$_2$-H)Cl$_2$], the methyl resonances (2:1 ratio) appear at 1.35 and 2.00 ppm while the amine hydrogen resonance appears at 5.2 ppm and the O---H---O hydrogen-bond resonance appears at 19.3 ppm. The slight shift in the O---H---O resonance is in the downfield direction as the O---O distance shortens from 2.474 (7) Å in the PnAO complex to 2.459 (2) Å in the AO complex. Additional studies of this correlation are under way.

The present and earlier comparison of AO and PnAO complexes of Rh(III) and other metal ions (Table VII) indicates that introduction of a propylene bridge opposite the hydrogen bond with metals of this approximate size, or smaller, imposes no significant constraint on the hydrogen bond. When they are compared with the corresponding Co(III) complexes,[2,3] however, significant lengthening of the hydrogen bond is found with the larger Rh(III) ion.

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Registry No. [Rh(PnAO-H)Cl$_2$], 88245-18-5; [Rh((AO)$_2$-H)Cl$_2$], 88245-19-6.

Supplementary Material Available: Listings of observed and calculated structure factors, temperature factor expressions, and hydrogen positional parameters for both complexes, intermolecular distances in [Rh(PnAO-H)Cl$_2$] (Table IV), and stereoscopic views of both unit cells (Figures 3 and 4) (35 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Physics,
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Structure and Magnetic Behavior of Iron(III) Dithiocarbamate Complexes Exhibiting $S = |{}^{1}/_{2}\rangle \rightleftarrows S = |{}^{5}/_{2}\rangle$ Thermal Equilibrium. Study of the Tris(*N*-methyl-*N*-*n*-butyldithiocarbamato)iron Homologue

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The molecular and crystal structures of the nonsolvated title complex have been determined at 300 K and its magnetic behavior has been studied by combined magnetic susceptibility measurement and Mössbauer spectroscopy in the temperature range between 300 and 77 K. The complex exhibits strong high–low-spin thermal equilibrium with a predominant contribution from the $S = |{}^{5}/_{2}\rangle$ state at high temperature and a drastic shift toward the $S = |{}^{1}/_{2}\rangle$ state at the low-temperature limit. Crystals are hexagonal $P3_1/c$, with a = 14.970 Å, c = 14.390 Å, V = 2792.8 Å^3, and Z = 4, and contain two independent complexes A and B, both sitting on the crystallographic threefold axis. The iron–sulfur bond distance $\langle$Fe–S$\rangle$ = 2.367 Å and the mean room-temperature effective magnetic moment μ_{eff}(300 K) = 4.72 μ_B are in good agreement with the corresponding values reported for other homologues also exhibiting high–low-spin thermal equilibrium.

Introduction

Complexes of octahedrally coordinated ferric ions can exist in two distinct spin states depending on the strength of the ligand field. Thus, in the presence of strong fields of O_h symmetry the term $^2T_{2g}$ ($t_{2g}{}^5$) lies lowest in energy and the iron ion is in the $S = {}^1/_2$ "low" spin state. The room-temperature value of the effective magnetic moment is in this case close to 2.0 μ_B, somewhat higher than the spin-only value μ_{eff} = 1.73 μ_B, due to the small contribution from the non-zero value of the orbital angular momentum in the $t_{2g}{}^5$ configuration.[1,2] Under weak ligand fields of O_h symmetry, on the other hand, the $^6A_{1g}$ ($t_{2g}{}^3e_g{}^2$) term becomes the ground state of the system with $S = {}^5/_2$ "high" spin and observed moments close to the spin-only value of 5.9 μ_B. Deviations from pure high- or low-spin behavior can arise in these and other complexes when the ligand field strength is comparable with the mean electron pairing energy of the d^5 configuration. In this case thermal equilibrium can be established between the two possible ground states $^2T_{2g}$ and $^6A_{1g}$, resulting in variation of the magnetic moments between the limiting values of 2.0 and 5.9 μ_B. Tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes constitute a typical class of molecules exhibiting high–low-spin thermal equilibrium. Magnetic susceptibility measurements, Mössbauer spectral behavior, and NMR shifts of numerous examples of these compounds have been successfully interpreted in terms of the $S = |{}^{1}/_{2}\rangle \rightleftarrows S = |{}^{5}/_{2}\rangle$ thermal equilibrium.[2-7] Failure to observe simultaneous population of both

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