cycle. Thus, both **1a** and **2** function as rudimentary chemical models for oxo-type molybdoenzymes, even though **1a** is coordinatively saturated.

Conclusions

The dithiophosphate complexes **1a** and **2** have been prepared and characterized by spectroscopic and crystallographic techniques. These six-coordinate complexes are further examples of oxo–Mo(IV) and dioxo–Mo(VI) complexes that undergo facile oxygen atom transfer reactions and catalyze the oxidation of PPh_3 by Me_2SO. The catalytic system described here employs the sterically encumbering $HB(Me_2pz)_3^-$ ligand to prevent Mo(V) dimer formation. Kinetic studies of the oxygen atom transfer reaction of **1a** and Me_2SO are interpreted in terms of dissociation of one sulfur atom of the η^2-dithiophosphate ligand to form an η^1-dithiophosphate complex prior to the transfer of an oxygen atom from Me_2SO to the Mo(IV) center. Oxygen atom transfer upon the nucleophilic attack of PPh_3 on the Mo(VI) center of **2** is followed by the rapid coordination of the second sulfur atom of the dithiophosphate ligand to form **1a**. As in previous systems[6,7] the coordination sphere of the Mo(VI) complex contains sulfur donor ligands. However, in contrast with previous systems[5,7] in which oxygen atom transfer to the Mo(IV) complex is facilitated by the presence of vacant coordination sites or labile solvent ligands on the metal center, both **1a** and **2** are six-coordinate. This study demonstrates that oxygen atom transfer may also be facilitated by changes in the denticity of ligands bound to the metal center.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (Grant No. GM-37773). The structure determinations were done with use of the facilities of the Molecular Structure Laboratory, Department of Chemistry, University of Arizona. ^{31}P NMR measurements were made by Dr. K. Christensen. GC/MS analyses were by M. Malcomson of the University Analytical Center of the University of Arizona.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated atomic positions, and bond distances and angles for $\{HB(Me_2pz)_3\}MoO\{S_2P(OEt)_2\}$ and $\{HB(Me_2pz)_3\}MoO_2\{S_2P(OEt)_2\}\cdot 0.5C_7H_8$ (7 pages); tables of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
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Structural Chemistry of Cobalt(III) Complexes of Thioacylhydrazide and Thioacylhydrazonate Ligands. Crystal Structures of $(-)_D$-*fac*-Tris(thioacethydrazide)cobalt(III) Chloride, $(-)_D$-*fac*-Tris(formaldehyde thioacethydrazidato)cobalt(III) Hydrate, and *fac*-Tris(thiosemicarbazide)cobalt(III) Chloride

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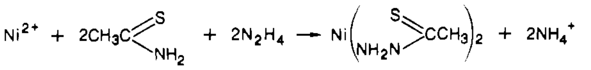
Thiosemicarbazide was found to be an excellent ligand for transition-metal ions by Jensen in 1934,[3] and since then coordination compounds of thiosemicarbazide have been studied intensively.[4] Simple thioacylhydrazides of aliphatic acids have been known for a few years, since they can be made by a metal ion assisted synthetic route. In the case of thioacethydrazide, the first step is the isolation of the sparingly soluble *trans*-bis(thioacethydrazidato)nickel(II), $Ni(tah)_2$:[5]



Bis(thioacethydrazidato)nickel(II) undergoes disproportionation on protonization with strong acids in water analogously to the behavior of the thiosemicarbazidato complex:[6]

$$3Ni(tah)_2 + 6H^+ \rightarrow Ni^{2+} + 2Ni(Htah)_3^{2+}$$

Tris(thioacethydrazide)nickel(II) chloride is easily isolated from the reaction mixture and may serve as a ligand donor to cobalt(III) in the unstable *trans*-dichlorotetrakis(pyridine)cobalt(III) perchlorate:[7]

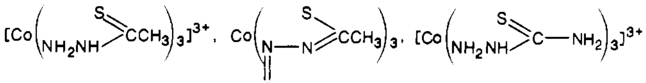
$$trans\text{-}Co(py)_4Cl_2^+ + Ni(Htah)_3^{2+} \rightarrow fac\text{-}Co(Htah)_3^{3+} + NiCl_2 + 4py$$

The free thioacethydrazide has been isolated according to the reaction scheme[8]

$$Ni(Htah)_3^{2+} + 2HO^- \rightarrow Ni(tah)_2 + Htah + 2H_2O$$

The formation of thiosemicarbazones and other hydrazones from the hydrazine derivative and an oxo compound is catalyzed by acid. It may therefore not be surprising that $Ni(Htsc)_3^{2+}$ and $Co(Htah)_3^{3+}$ react readily with aldehydes and ketones. In some cases it has even been possible to make coordination compounds of thioacylhydrazones that are otherwise unknown.[9,10]

The present structure determinations were performed to obtain an understanding of the degree of delocalization in the three ligand systems



and to establish with certainty the absolute configuration of the two chiral coordination compounds.

Experimental Section

Preparation of Compounds. Δ-*fac*-$(-)_D$-$Co(Htah)_3Cl_3$ (I) was obtained according to published methods.[7] Δ-*fac*-$(-)_D$-$Co(CH_2{=}tah)_3\cdot H_2O$ was prepared from this product. A 1.2-g amount of I was dissolved in hot water (12 mL), and after cooling to room temperature, 12 mL of 35% aqueous formaldehyde was added. The desired product precipitated during 5 h. *fac*-$Co(Htsc)_3Cl_3$ was obtained as described in the literature.[11] It has been reported to be isostructural with the rhodium complex.[12]

X-ray Crystallography. The three crystal structures were determined by the heavy-atom method and refined by least squares, minimizing $\sum w(|F_o| - |F_c|)^2$. Table I contains a summary of the crystal data as well as some details for the data collection and structure refinements. The positional parameters for the non-hydrogen atoms in the structures are

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(1) Royal Veterinary and Agricultural University.
(2) H. C. Ørsted Institute.
(3) Jensen, K. A.; Rancke-Madsen, E. *Z. Anorg. Allg. Chem.* **1934**, *219*, 243.
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(7) Gabel, J.; Larsen, E. *Acta Chem. Scand., Ser. A* **1978** *A32*, 929.
(8) Jensen, K. A.; Larsen, E. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 137.
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(12) Samus, I. D. *Koord. Khim.* **1981**, *7*, 120.

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Table I. Crystallographic Data

	I	II	III
formula	$CoC_6H_{18}N_6S_3Cl_3$	$CoC_9H_{17}N_6OS_3$	$CoC_3H_{15}N_9S_3Cl_3$
molar mass/g mol^{-1}	435.73	380.4	438.68
cryst system	cubic	monoclinic	monoclinic
space group	$P2_13$	$C2$	$P2_1/c$
temp/K	296 (1)	105 (1)	105 (1)
cell params			
a/Å	12.003 (3)	26.917 (7)	15.169 (3)
b/Å		6.488 (2)	11.595 (2)
c/Å		9.381 (2)	9.029 (2)
β/deg		102.68 (2)	101.9 (10)
V/Å^3	1729.3 (13)	1598.3 (14)	1557.9 (10)
Z	4	4	4
d_{calcd}/g cm^{-3}	1.674	1.581	1.870
diffractometer	Picker FACS-1	CAD 4	CAD 4
μ(Mo Kα)/cm^{-1}	18.026	14.512	20.375
developed faces	$[111]$, $[11\bar{1}]$, $[1\bar{1}\bar{1}]$, $[1\bar{1}1]$	$[100]$, $[010]$, $[001]$, $[201]$, $[20\bar{1}]$	$[100]$, $[011]$
transmission factors	0.6042–0.7205	0.7581–0.8510	0.6043–0.7863
cryst size/mm^3	0.042 × 0.042 × 0.042	0.1 × 0.2 × 0.35	0.10 × 0.23 × 0.24
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ limits/deg	1.2–27.5	1–35	1–32.2
octants measd	h,k,l	$h,-k,\pm l$	$\pm h,k,l$
no. of reflcns^a	759, 730	3772, 3179	5481, 3910
R, R_w	0.020, 0.025	0.023, 0.029	0.024, 0.029
no. of variables	76	249	232
wt/$w^{-1\,b}$	$3\sigma^2(F) + 0.0007F^2$	$\sigma^2(F) + 0.0005F^2$	$1.5\sigma^2(F) + 0.0005F^2$
largest shift^c	0.2σ	0.3σ	0.03σ
max peak/e Å$^{-3\,c}$	0.3	0.6	0.4

^{a} Unique and observed reflections with $|F^2| \geq 2\sigma(|F|^2)$. ^{b} $\sigma(|F|^2)$ calculated from counting statics. ^{c} Largest shift during the final refinement cycle giving the maximum peak in the final $\Delta\rho$ map.

Table II. Positional parameters for Non-Hydrogen Atoms in I

atom	x	y	z
Co	0.04489 (2)	0.044 89	0.044 89
S	0.02641 (5)	0.062 39 (5)	−0.137 66 (5)
N1	0.0322 (2)	0.210 5 (2)	0.054 5 (2)
N2	0.0260 (2)	0.262 4 (2)	−0.052 4 (2)
C1	0.0216 (2)	0.203 4 (2)	−0.142 8 (2)
C2	0.0147 (3)	0.261 2 (3)	−0.252 4 (3)
C11	0.22693 (6)	0.226 93	0.226 93
C12	0.47818 (5)	0.478 18	0.478 18
C13	0.32232 (6)	0.177 68	0.822 32

Table III. Positional Parameters for Non-Hydrogen Atoms in II

atom	x	y	z
Co	0.132 68 (1)	0.25000	0.10041 (3)
S1	0.179 25 (2)	0.06303 (9)	0.27729 (5)
S2	0.068 92 (2)	0.03546 (9)	0.10303 (6)
S3	0.157 25 (2)	0.05494 (9)	−0.06442 (5)
N11	0.194 16 (6)	0.4210 (3)	0.1169 (2)
N12	0.238 45 (7)	0.3756 (3)	0.2257 (2)
C11	0.233 68 (7)	0.2122 (3)	0.3005 (2)
C12	0.278 84 (9)	0.1466 (5)	0.4162 (3)
C13	0.200 85 (8)	0.5728 (4)	0.0352 (2)
N21	0.105 82 (6)	0.4102 (3)	0.2433 (2)
N22	0.064 46 (7)	0.3332 (3)	0.2981 (2)
C21	0.046 50 (7)	0.1605 (4)	0.2392 (2)
C22	0.004 09 (8)	0.0613 (5)	0.2949 (3)
C23	0.121 96 (8)	0.5860 (3)	0.2979 (2)
N31	0.093 65 (7)	0.4050 (3)	−0.0676 (2)
N32	0.101 11 (7)	0.3623 (3)	−0.2096 (2)
C31	0.129 36 (8)	0.2009 (3)	−0.2141 (2)
C32	0.137 25 (10)	0.1345 (4)	−0.3611 (2)
C33	0.060 09 (9)	0.5446 (4)	−0.0663 (2)
O1	0.456 33 (14)	0.0907 (6)	0.4619 (4)
O2	0.437 93 (13)	0.1894 (6)	0.4305 (4)

listed in Tables II–IV. The supplementary material contains tables of anisotropic thermal parameters, parameters for the hydrogen atoms, structure factors, possible hydrogen bonds, and complete bond distances and angles.

Δ-*fac*-Co(Htah)$_3$Cl$_3$ (I). The compound crystallizes as optically isotropic, red, pyramidal crystals. The Laue symmetry of the diffraction pattern and the systematically absent reflections, $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, are only consistent with the space group $P2_13$.

Table IV. Positional Parameters for Non-Hydrogen Atoms in III

atom	x	y	z
Co	0.250 96 (2)	0.476 28 (2)	0.19746 (3)
S1	0.156 22 (3)	0.419 96 (4)	−0.01055 (5)
S2	0.173 03 (3)	0.379 30 (4)	0.34174 (5)
S3	0.334 79 (3)	0.320 53 (4)	0.19084 (5)
C1	0.101 74 (11)	0.550 5 (2)	−0.0487 (2)
N11	0.174 19 (10)	0.615 47 (13)	0.1931 (2)
N12	0.119 63 (11)	0.636 53 (14)	0.0493 (2)
N13	0.043 76 (11)	0.567 98 (16)	−0.1761 (2)
C2	0.217 47 (11)	0.447 6 (2)	0.5085 (2)
N21	0.327 70 (10)	0.532 07 (14)	0.3891 (2)
N22	0.283 05 (10)	0.524 08 (15)	0.5133 (2)
N23	0.186 18 (11)	0.425 7 (2)	0.6323 (2)
C3	0.389 85 (11)	0.365 82 (15)	0.0518 (2)
N31	0.330 26 (10)	0.551 28 (14)	0.0752 (2)
N32	0.370 34 (11)	0.469 92 (14)	−0.0106 (2)
N33	0.447 90 (11)	0.298 62 (15)	0.0023 (2)
C11	0.521 24 (3)	0.562 44 (4)	0.29629 (5)
C12	0.323 46 (3)	0.801 07 (4)	0.28349 (5)
C13	0.018 32 (3)	0.845 25 (4)	−0.11319 (6)

The setting angles for 28 reflections with θ values between 20 and 22° were used in a least-squares refinement of the cell constants and the orientation matrix. The intensities for three standard reflections were recorded after every 60 reflections. These measurements decreased with exposure time during the data collection by a total of 7%. The data were corrected for Lorentz, polarization, and absorption[13] effects. A scaling function linear in exposure time was used to correct for the decrease in intensity.

Structure Determination and Refinement. The X-Ray System[14] was used for the crystallographic calculations. The cobalt atom and the three chloride ions are located on the 3-fold axes of symmetry. The positions for the hydrogen atoms were located in a difference density map calculated after anisotropic refinement of the non-hydrogen atoms. The atomic scattering factors were taken from the Cromer and Waber tabulation,[15] with the values for the neutral atoms being used, except for hydrogen, where the values of Stewart et al. were employed.[16] The

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(13) Coppens, P.; Leiserowitz, L.; Rabinowitch, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(14) "X-Ray System"; Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

(15) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table V. Bond lengths (Å) and Bond Angles (deg) in I and Averaged Values for II and III

	I	II	III
Co–S	2.2123 (8)	2.2108 (8)	2.2241 (7)
Co–N1	1.997 (2)	1.964 (2)	1.989 (2)
S-C1	1.694 (3)	1.727 (2)	1.722 (2)
C1–N2	1.300 (3)	1.296 (3)	1.331 (3)
N1–N2	1.428 (3)	1.418 (3)	1.423 (3)
C1–C2(N3)	1.470 (4)	1.502 (4)	1.320 (3)
S–Co–N1	87.41 (6)	85.52 (6)	86.45 (5)
S–Co–S′	90.24 (2)	89.29 (3)	90.21 (2)
S–Co–N1′	177.3 (2)	174.7 (2)	175.8 (3)
S–Co–N1′	91.08 (6)	91.24 (6)	92.17 (5)
N1′–Co–N1″	91.32 (8)	93.99 (7)	91.33 (6)
Co–S–C1	97.71 (9)	96.40 (7)	97.01 (6)
S–C1–N2	121.0 (2)	124.6 (2)	119.62 (14)
S–C1–C2(N3)	119.9 (2)	117.8 (2)	127.02 (14)
N2–C1–C2(N3)	119.1 (2)	117.6 (2)	119.3 (2)
C1–N2–N1	121.0 (2)	113.3 (2)	118.4 (2)
Co–N1–N2	112.73 (14)	119.8 (2)	112.52 (11)

atomic scattering factors for Co, S, and Cl were corrected for the effects of anomalous dispersion by using the values of Cromer and Liberman.[17] The coefficients in the weighting function were selected to give a uniform distribution of $\langle w(\Delta F)^2 \rangle$ vs $|F_o|$ and sin θ. The absolute configuration of the cation was established with a probability larger than 0.999 by using Hamilton's R value test as described by Rogers.[18]

During the final refinement cycles, the 76 variables refined were the scale factor, positional and anisotropic thermal parameters for the non-hydrogen atoms, and the positional parameters for the hydrogen atoms. A common isotropic thermal parameter of 0.07 Å^2 was used for the hydrogens. An analysis of the values of $|F_o|$ and $|F_c|$ showed that no correction for secondary extinction was required.

Δ-*fac*-Co(CH$_2$=tah)$_3$·H$_2$O (II). The red crystals obtained by slow precipitation of the formaldehyde condensation product are elongated in the direction of the b axis. Preliminary Weissenberg and precession photographs showed that the crystals belong to the monoclinic system. The systematically absent refletions, hkl, $h + k = 2n + 1$, are consistent with the space groups $C2$, Cm, and $C2/m$. The last two could be excluded as the compound is optically active. An Enraf-Nonius gas-flow low-temperature device was used for the collection of intensity data. The temperature was measured to 105 (1) K with a thermocouple. The cell parameters and the orientation matrix were obtained from the setting angles for 19 reflections with θ values in the range 11–20°. On the basis of a detailed profile analysis of the strong reflections, the ω–2θ scan type was selected as the most suitable for the data collection. The intensities for three standard reflections were monitored every 10 000 s. These measurements showed no systematic variation. The data reduction and structure solution and refinement were performed as described for compound I. The y coordinate for Co was fixed during all the refinement cycles. After all non-hydrogen atoms had been located, the difference Fourier map revealed two major maxima separated by 0.8 Å. These peaks were interpreted as two partly populated positions for the water oxygen atom. The possible hydrogen bonds involving the water molecules were analyzed, and the only system that had donor–acceptor distances in the normal range had the two water positions equally populated. No deviation from monoclinic symmetry was observed in the diffraction pattern, indicating that this arrangement cannot be described as an ordered structure of lower symmetry. Consequently, the population parameters were fixed at 0.5 during the remaining refinement cycles. The positions of the hydrogen atoms in the complex were found in the difference density map calculated after an anisotropic refinement, but it was impossible to locate the hydrogen atoms of the partly populated water molecules.

***fac*-Co(Htsc)$_3$Cl$_3$ (III).** This compound crystallizes from water as red rhombic plates. On the basis of Weissenberg and precession photographs, the crystals were assigned to the monoclinic system. The systematically absent reflections, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), are only consistent with the space group $P2_1/c$. The data collection and reduction and the structure refinement followed the same procedure as described for II. For III, 18 reflections with θ values between 19 and 24° were used to determine the orientation matrix and the unit cell dimensions. The intensities of three standard reflections monitored during the data collection showed no systematic variation.

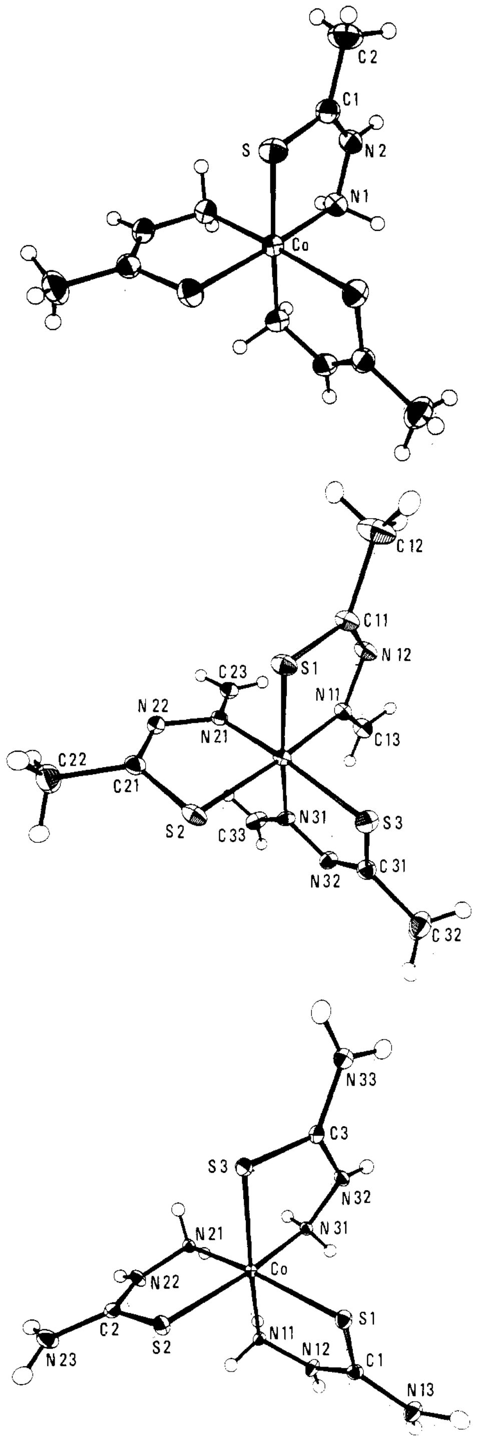

Figure 1. ORTEP drawings of the three cobalt(III) coordination compounds illustrating the atomic labeling: (a, top) Δ-(−)$_D$-*fac*-Co(Htah)$_3$$^{3+}$; (b, middle) Δ-(−)$_D$-Co(CH$_2$=tah)$_3$; (c, bottom) Co(Htsc)$_3$$^{3+}$. The thermal ellipsoids are scaled to include 50% probabilities. The hydrogen atoms are drawn as spheres with a radius of 0.1 Å.

Description of the Crystal Structures

Δ-(−)$_D$-*fac*-Co(Htah)$_3$Cl$_3$. The cation has 3-fold symmetry as illustrated in Figure 1a. Bond lengths and angles for non-hydrogen atoms are listed in Table V. The distances from the atoms S, C1, N2, and N1 to a least-squares plane defined by these atoms are 0.003, −0.007, 0.007, and −0.003 Å, respectively. The methyl carbon atom, C2, is contained in the ligand plane, while the Co atom has a distance of 0.102 Å to the plane. The cations and the chloride ions are linked by hydrogen bonds in the crystal with normal N–Cl distances in the range 3.129–3.215 Å.

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(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(18) Rogers, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A35*, 734.

Δ-$(-)_D$-*fac*-Co(CH_2=tah)$_3\cdot H_2O$. The molecular structure is depicted in Figure 1b. The three ligands are planar. Least-squares planes through S, C, N, and N of each ligand have been calculated. The cobalt atom is only 0.066 Å out of the plane defined by S1, C11, N11, and N12 but 0.13 and 0.21 Å out of the planes defined by the two other ligands. The planes A, B, and C defined in this way form the angles A/B = 82.4°, A/C = 86.9°, and B/C = 78.0°. Both substituents of the chelate rings are displaced relative to the least-squares planes. The carbon atoms of the methylene groups show the largest distances, 0.11, −0.07, and −0.18 Å, respectively, for the three ligands. The pronounced deviation from 3-fold symmetry has been found to originate in the intermolecular interactions.

***fac*-Co(Htsc)$_3$Cl$_3$.** The cation is shown in Figure 1c. The packing arrangement for this compound is also determined by extensive hydrogen bonding between all the nitrogen-bound hydrogen atoms and chloride ions. The N–Cl distances are found to be between 3.1 and 3.5 Å. Hydrogen atoms on N32 and N21 form bifurcated hydrogen bonds to the chloride ions as formerly observed between $-NH_2$ groups and oxygen atoms.[19] The least-squares planes defined by the atoms S, C, N, and N of the three chelate backbones were calculated. The four atoms of the ligand in III have distances to the plane of −0.042, 0.095, and −0.103 Å, respectively, illustrating a small but significant puckering of this ligand. The two other ligands are planar, similar to what was observed in structures I and II. The difference between the ligand in Co(Htsc)$_3$Cl$_3$ and the other two is also reflected in the molecular dimensions of the ligand. The C3–N32 bond of 1.341 (2) Å is significantly longer than the two corresponding distances of 1.327 (2) and 1.325 (2) Å. The cobalt atom has distances to the three ligand planes varying between 0.46 and 0.51 Å. The angles for the three planes are calculated to be A/B = 82.7°, A/C = 61.6°, and B/C = 64.6°. It seems likely that the extensive hydrogen bonding is causing the irregularities of the coordination cation.

Discussion

Co(Htah)$_3$Cl$_3$ is the only compound of the three studied that possesses a 3-fold axis of symmetry in the crystal. In the two other structures the relative arrangement of the chelate rings does not show 3-fold symmetry, as demonstrated by the rather different angles between the planes defined by the backbone of each chelate. The packing arrangements in II and III are strongly influenced by hydrogen bonding, and this seems to be the plausible cause for the lack of 3-fold symmetry in these compounds. The molecular dimensions observed in the three independent chelate ligands of II and III do not differ grossly, and the averaged bond lengths and angles are listed in Table V.

In Co(Htah)$_3^{3+}$, S, C1, and N2 seem to participate in the π-bonding system and the C–S bond (1.694 (3) Å) has a value close to the distance of a C–S double bond.[20] In Co(CH_2=tah)$_3$, the chain of S, C1, N2, N1, and C3 forms the π-system, and consequently the C–S bond (1.727 (4) Å) is elongated compared to that of Co(Htah)$_3^{3+}$. The N1–N2 distance also reflects the effect of the conjugation, being longer (1.428 (3) Å) in I, where a pure single bond is expected, and shorter (1.418 (2) Å) in II, where the bond is participating in the conjugated system. In Co(Htsc)$_3^{3+}$ the conjugation is clearly dominated by the bond between the amide nitrogen and the carbon atom, as indicated by the long C–S bond length of 1.7222 (4) Å compared to the bond distance 1.688 (4) Å found for I.

The absolute configurations of the $(-)_D$-*fac*-tris(thioacethydrazide)cobalt(III) ion and of $(-)_D$-*fac*-tris(formaldehyde thioacethydrazonato)cobalt(III) have here been determined to be Δ, in agreement with an earlier assignment based on circular dichroism spectroscopy.[8] In the visible region $(-)_D$-Co(Htah)$_3^{3+}$ exhibits an absorption band at ca. 500 nm due to the lowest lying spin-allowed transition. In connection with this, a single circular dichroism band of negative sign is observed. This would imply the Δ absolute configuration according to an empirical correlation that, however, is known to have exceptions.[21] In the UV region these compounds exhibit a series of absorption bands with varying molar absorption coefficients up to 30 000 M^{-1} cm^{-1}. The allowed transitions giving rise to these bands are interpreted as ligand to metal charge-transfer and internal ligand π to π^* transitions. The latter transitions are expected to show exciton splitting of the absorption band combined with relatively intense Cotton effects. However, with unsymmetric bidentate chelates the symmetry allows extensive mixing of transitions and the spectroscopic determination of the absolute configuration becomes unreliable. The present determination of the absolute configurations is therefore in this case considered a necessity.

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Registry No. I, 69799-63-9; II, 115227-31-1; III, 29855-60-5; Htah, 62543-18-4; formaldehyde, 50-00-0.

Supplementary Material Available: For Δ-Co(Htah)$_3$Cl$_3$, listings of anisotropic thermal parameters (Table SI), hydrogen positions (Table SII), and possible hydrogen bonds (Table SIV), for Δ-Co(CH_2=tah)$_3\cdot H_2O$, listings of anisotropic thermal parameters (Table SV), hydrogen positions and thermal parameters (Table SVI), bond lengths and angles (Table SVIII), and possible hydrogen bonds (Table SIX), and for *fac*-Co(Htsc)$_3$Cl$_3$, listings of anisotropic thermal parameters (Table SX), hydrogen positions and thermal parameters (Table SXI), bond lengths and angles (Table SXIII) and possible hydrogen bonds (Table SXIV) (10 pages); listings of observed and calculated structure amplitudes (Tables SIII, SVII, and SXII) (43 pages). Ordering information is given on any current masthead page.

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Molecular Dinitrogen Complexes of Ruthenium(II) Porphyrins

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Binding of dinitrogen at a ruthenium(II) porphyrin center was first noted by Hopf and Whitten,[3] but the reaction, monitored only by UV/visible spectral changes, involved surfactant species in monolayer assemblies. Subsequent to this, UV/visible studies suggested in situ formation of a dinitrogen complex following exposure of Ru(OEP)(DMF)$_2$ to N_2.[4,5] Later, the labile Ru(OEP)(THF)(N_2) complex was isolated ($\nu(N_2)$ = 2110 cm^{-1}).[6] The existence of such species was questioned at one time,[7] but recent work on Ru(TMP) systems has fully established the existence of both mono- and bis(dinitrogen) complexes.[8] Here we

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