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Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Hindered-Ligand Systems. 9. Structure of the *cis,cis*-1,3,5-Tris(pyridine-2-carboxaldimino)cyclohexane Complexes of Cobalt(II) and Zinc(II) Ions

R. A. D. WENTWORTH,* P. S. DAHL, C. J. HUFFMAN, W. O. GILLUM, W. E. STREIB, and J. C. HUFFMAN*

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The title compounds are isostructural and adopt approximate trigonal-prismatic coordination in the solid state. Distortions from ideal C_{3v} symmetry are due to a combination of intra- and intermolecular nonbonded contacts. The perchlorate salts of the two complexes are isomorphous, space group $P2_1/c$, with cell dimensions of $a = 13.421$ (12) Å, $b = 13.731$ (10) Å, $c = 15.213$ (12) Å, and $\beta = 109.71$ (5)° for Co and $a = 13.440$ (5) Å, $b = 13.738$ (5) Å, $c = 15.279$ (6) Å, and $\beta = 109.89$ (4)° for Zn. Final residuals for diffractometer-collected data are $R = 0.079$ and $R_w = 0.033$ for Co and $R = 0.042$ and $R_w = 0.053$ for Zn.

Introduction

The natural conformation of the ligand 1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane ((py)$_3$tach) is one in which the nitrogen atoms occupy the vertices of a trigonal prism if the substituents of the cyclohexane ring occupy axial sites. The structure of the cation in [Zn((py)$_3$tach)](ClO$_4$)$_2$ has indeed been shown[1] by us to consist of a slightly tapered trigonal prism and constituted the first complex with innocent ligands in which this structure was observed. We have also shown[2] from X-ray powder patterns that the Mn(II), Co(II), and Zn(II) complexes are isomorphous while the Ni(II) complex is unique. Since no ligand field stabilization energy is accrued by either a d^{10} or a high-spin d^5 complex in either trigonal-prismatic or octahedral geometries, it is likely that the Zn(II) and Mn(II) complexes are isostructural. On the other hand, the differences in energies of an octahedral and trigonal-prismatic high-spin d^7 complex is[3] $-{}^{10}/{}_{3}Dq + 3B$ with B being the customary Racah parameter. With use of parameters gleaned from Co(bpy)$_3^{2+}$, this difference in energies can be estimated[3] to be about 5 kcal mol^{-1}. The slight energetic preference for an octahedral structure in terms of the electronic configurations could be easily overcome by the geometric preference of the hindered ligand allowing the Co(II) complex to adopt the geometry of a trigonal prism. In contrast, the same difference in energies for a d^8 complex is[3] $-{}^{20}/{}_{3}Dq - 3B$, and we have estimated that the preference for an octahedral structure in terms of the electronic structure probably amounts to about 30 kcal mol^{-1} (on the basis of parameters from Ni(bpy)$_3^{2+}$). The magnitude of this electronic preference for an octahedral geometry should be sufficient to compete with the ligand's preference for trigonal-prismatic coordination. Indeed, the average twist angle in the Ni(II) complex has been shown[4] to be about 32°.

Since the validity of our estimates with the Co(II) complex remained to be seen, we undertook and report herein the structure of [Co((py)$_3$tach)](ClO$_4$)$_2$. We also include some of the heretofore unpublished parameters from [Zn((py)$_3$tach)](ClO$_4$)$_2$.

Results and Discussion

An ORTEP drawing of Co((py)$_3$tach)$^{2+}$ showing the numbering scheme used is illustrated in Figure 1. The fact that the Co(II) and Zn(II) complexes are isostructural is amply illustrated in Table I, which gives the distance from atoms in one ion to the corresponding atoms in the other ion after the atomic coordinates of the Zn((py)$_3$tach)$^{2+}$ ion have been translated and rotated within the cell of the Co(II) ion to obtain a least-squares fit.[5] Bond distances and angles within the coordination environment for the two complexes are compared in Table II, and the average values for all remaining molecular parameters are shown in Figure 2. One disturbing feature of the molecular parameters is the discrepancy in what should be "chemically equivalent" distances within the coordination sphere. This is especially true in M–N(pyridyl) distances, which differ up to 18σ while the maximum deviation in the "chemically equivalent" molecular parameters of the ligand is only 5σ. The distortions present are best illustrated in Figure 3, a view down the approximate threefold axis of the molecule, and Table III, a least-squares analysis of the pyridine-2-carboxaldimino planes in the ligand.

Table I. Least-Squares Fit of Spatial Coordinates of Zn((py)$_3$tach)$^{2+}$ onto Co((py)$_3$tach)$^{2+}$

atom	Δd, Å	atom	Δd, Å	atom	Δd, Å
M	0.016	C(5)	0.028	C(15)	0.037
N(1)	0.029	C(6)	0.052	C(16)	0.040
N(2)	0.017	C(7)	0.067	C(17)	0.013
N(3)	0.045	C(8)	0.046	C(18)	0.045
N(4)	0.020	C(9)	0.029	C(19)	0.027
N(5)	0.017	C(10)	0.046	C(20)	0.022
N(6)	0.057	C(11)	0.022	C(21)	0.017
C(1)	0.053	C(12)	0.033	C(22)	0.034
C(2)	0.009	C(13)	0.027	C(23)	0.033
C(3)	0.044	C(14)	0.048	C(24)	0.011
C(4)	0.015				

Table II. Some Bond Distances (Å) and Angles (Deg) within the Immediate Coordination Environment of Co((py)$_3$tac)$^{2+}$ and Zn((py)$_3$tach)$^{2+}$

	Co	Zn
d(M–N(1))	2.206 (7)	2.211 (4)
d(M–N(3))	2.243 (7)	2.282 (4)
d(M–N(5))	2.246 (7)	2.258 (4)
d(M–N(2))	2.141 (7)	2.148 (4)
d(M–N(4))	2.125 (7)	2.142 (4)
d(M–N(6))	2.128 (7)	2.167 (4)
N(1)–M–N(3)	91.4 (3)	91.6 (1)
N(3)–M–N(5)	89.6 (2)	89.9 (1)
N(5)–M–N(1)	93.4 (3)	94.4 (2)
N(2)–M–N(4)	82.9 (3)	83.2 (2)
N(4)–M–N(6)	80.4 (3)	81.2 (2)
N(6)–M–N(2)	82.9 (3)	83.3 (2)
N(1)–M–N(2)	75.7 (3)	75.2 (1)
N(3)–M–N(4)	74.2 (3)	73.8 (1)
N(5)–M–N(6)	75.2 (3)	73.9 (2)

In order to explain these discrepancies, we undertook a careful analysis of nonbonded interactions. Hydrogen positions

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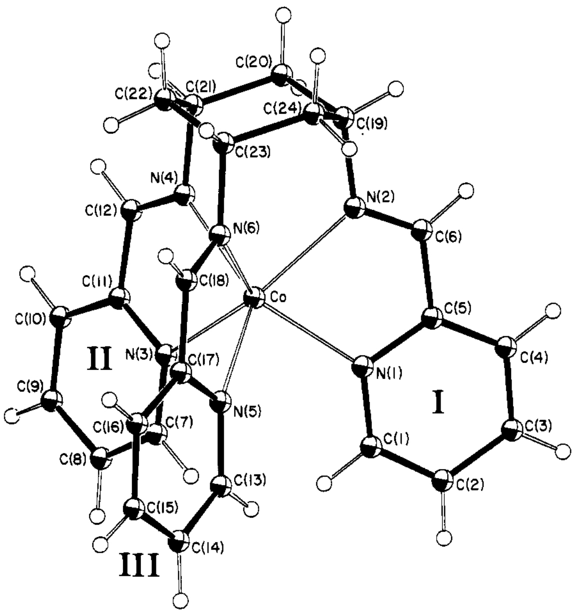

Figure 1. ORTEP drawing of Co((py)$_3$tach)$^{2+}$ ion showing numbering scheme used.

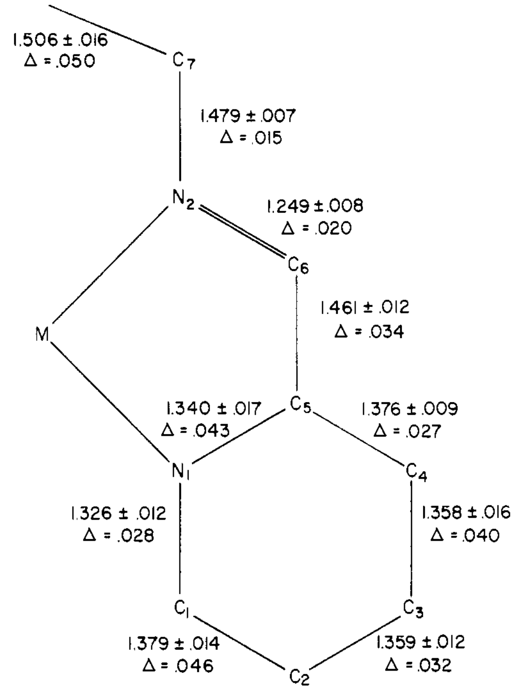

Figure 2. Schematic drawing of pyridine-2-carboxaldimino section of (py)$_3$tach with average distances and numbering scheme used in least-squares planes definitions.

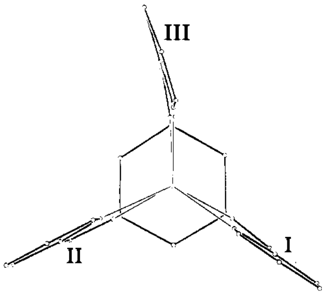

Figure 3. View down pseudo-three-fold axis of Co((py)$_3$tach)$^{2+}$ ion showing definitions used in least-squares planes analysis.

Table III. Least-Squares Planes Analysis[a]

	Zn			Co		
atom[a]	I	II	III	I	II	III
N_1[b]	−0.005	−0.009	−0.032	0.001	−0.005	−0.031
C_1[b]	0.001	−0.003	0.016	−0.012	−0.006	0.011
C_2[b]	0.005	0.011	0.015	0.012	0.010	0.019
C_3[b]	−0.006	−0.007	−0.030	−0.002	−0.003	−0.031
C_4[b]	0.002	−0.004	0.014	−0.010	−0.008	0.011
C_5[b]	0.004	0.012	0.017	0.011	0.013	0.020
N_2	0.068	0.038	−0.078	0.060	0.015	−0.076
C_6	−0.008	0.019	0.061	0.008	−0.006	0.076
C_7	0.007	−0.004	−0.058	0.003	−0.056	−0.020
M	−0.027	0.037	−0.572	−0.027	0.062	−0.548

[a] See Figure 2 for atom nomenclature; planes are defined in Figure 3. [b] Atoms used to define plane.

Table IV. Nonbonded Distances (Å)

	Co	Zn
H(C1)···H(C7)	1.99	1.97
H(C7)···H(C13)	1.95	1.94
H(C1)···H(C13)	2.23	2.17

Table V. Crystal Data

	Co	Zn
space group	$P2_1/c$	$P2_1/c$
cell dimens (20 °C)		
a, Å	13.421 (12)	13.440 (5)
b, Å	13.731 (10)	13.738 (5)
c, Å	15.213 (12)	15.279 (6)
β, deg	109.71 (5)	109.89 (4)
V, Å^3	2639.3	2652.9
Z	4	4
D_{calcd}, g cm^{-3}	1.647	1.654
μ(Mo Kα), cm^{-1}	9.109	12.087

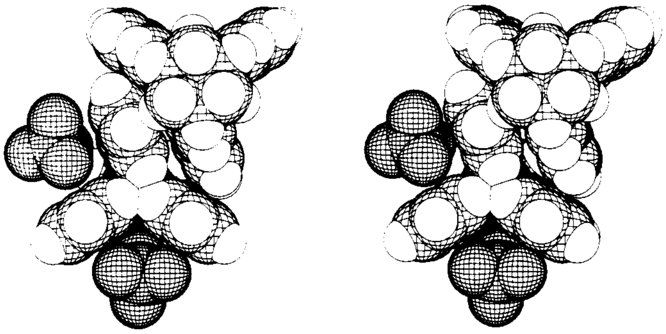

Figure 4. Stereo space-filling-model drawing of packing of Co((py)$_3$tach)$^{2+}$ [ClO$_4^-$]$_2$. The cation to the upper right has the cyclohexane toward the viewer, and the other cation is related to the first by an inversion center. Only two perchlorate ions are shown.

were calculated for idealized geometries[6] with d(C–H) = 1.08 Å. It was immediately obvious that the interactions of H(C1), H(C7), and H(C13) were largely responsible for the "twist" distortions present, as shown in Table IV. The shortest H···H contacts other than those involving H(C1), H(C7), and H(C13) were greater than 2.35 Å. There were still some questions as to why a symmetrical twist was not present, and this was finally resolved in the space-filling-model drawing of the packing shown in Figure 4. In Figure 4 it is seen that plane III is forced into the side of plane II, while plane I is loosely surrounded by perchlorate ions.

The only remaining question is the rather large discrepancy in M–N distances. This we explain by noting that the centroid[7] (C_t) of the six coordinating nitrogens also show large deviations in C_t–N distances, ranging from 2.06 to 2.29 Å for the Co(II)

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(6) Hydrogen positions were calculated with a local version of J. A. Ibers' HYDRA program, Northwestern University, Evanston, IL.

(7) The centroid is defined simply as the unweighted average of the spatial coordinates of the points in question.

Table VI. Fractional Coordinates for $Co((py)_3tach)^{2+}$ and $Zn((py)_3tach)^{2+}$ Perchlorates

	Co			Zn		
atom	*x*	*y*	*z*	*x*	*y*	*z*
M	0.2595 (1)	0.5048 (1)	0.2979 (1)	0.2611 (1)	0.5064 (1)	0.2987 (1)
N(1)	0.3155 (7)	0.6565 (6)	0.3048 (6)	0.3158 (3)	0.6570 (3)	0.3059 (3)
N(2)	0.1500 (6)	0.5860 (6)	0.3440 (5)	0.1512 (3)	0.5877 (3)	0.3443 (3)
N(3)	0.2904 (7)	0.4795 (6)	0.1638 (6)	0.2912 (3)	0.4817 (3)	0.1622 (3)
N(4)	0.1188 (7)	0.4413 (6)	0.2052 (6)	0.1201 (3)	0.4412 (3)	0.2055 (3)
N(5)	0.4211 (7)	0.4463 (7)	0.3774 (5)	0.4231 (3)	0.4462 (3)	0.3782 (3)
N(6)	0.2329 (7)	0.3960 (6)	0.3871 (6)	0.2374 (3)	0.3460 (3)	0.3910 (3)
C(1)	0.3977 (9)	0.6954 (8)	0.2872 (9)	0.3989 (5)	0.6986 (4)	0.2904 (5)
C(2)	0.4205 (9)	0.7945 (9)	0.2958 (9)	0.4220 (5)	0.7951 (4)	0.2971 (4)
C(3)	0.3548 (10)	0.8551 (7)	0.3197 (7)	0.3567 (4)	0.8587 (4)	0.3208 (4)
C(4)	0.2696 (9)	0.8188 (8)	0.3367 (7)	0.2711 (4)	0.8201 (4)	0.3382 (4)
C(5)	0.2524 (8)	0.7202 (8)	0.3303 (7)	0.2526 (4)	0.7225 (4)	0.3307 (3)
C(6)	0.1638 (8)	0.6759 (8)	0.3476 (6)	0.1616 (4)	0.6776 (4)	0.3470 (3)
C(7)	0.3736 (9)	0.4980 (11)	0.1401 (8)	0.3735 (4)	0.5027 (6)	0.1382 (4)
C(8)	0.3803 (10)	0.4824 (12)	0.0520 (10)	0.3779 (5)	0.4855 (6)	0.0505 (4)
C(9)	0.2956 (12)	0.4430 (9)	−0.0149 (8)	0.2958 (6)	0.4436 (4)	−0.0149 (4)
C(10)	0.2098 (9)	0.4231 (8)	0.0076 (8)	0.2078 (5)	0.4212 (4)	0.0079 (4)
C(11)	0.2081 (9)	0.4431 (7)	0.0955 (8)	0.2092 (4)	0.4429 (4)	0.0971 (4)
C(12)	0.1176 (9)	0.4222 (8)	0.1249 (8)	0.1175 (4)	0.4209 (4)	0.1253 (4)
C(13)	0.5160 (11)	0.4713 (9)	0.3742 (7)	0.5180 (4)	0.4702 (4)	0.3743 (4)
C(14)	0.6055 (9)	0.4151 (11)	0.4085 (9)	0.6061 (4)	0.4122 (5)	0.4073 (4)
C(15)	0.5982 (10)	0.3269 (10)	0.4483 (8)	0.5973 (5)	0.3253 (5)	0.4468 (4)
C(16)	0.5039 (11)	0.3035 (8)	0.4573 (7)	0.5034 (5)	0.3019 (4)	0.4574 (4)
C(17)	0.4170 (9)	0.3639 (8)	0.4223 (7)	0.4187 (4)	0.3639 (4)	0.4228 (3)
C(18)	0.3128 (10)	0.3447 (8)	0.4296 (7)	0.3154 (4)	0.3430 (4)	0.4318 (4)
C(19)	0.0566 (9)	0.5421 (7)	0.3583 (8)	0.0567 (4)	0.5434 (4)	0.3578 (4)
C(20)	−0.0166 (7)	0.5033 (9)	0.2653 (7)	−0.0159 (4)	0.5044 (5)	0.2650 (4)
C(21)	0.0263 (9)	0.4151 (9)	0.2317 (7)	0.0273 (4)	0.4147 (4)	0.2328 (4)
C(22)	0.0559 (9)	0.3380 (8)	0.3040 (9)	0.0589 (4)	0.3382 (4)	0.3067 (4)
C(23)	0.1295 (10)	0.3729 (9)	0.3965 (9)	0.1332 (4)	0.3738 (4)	0.3988 (4)
C(24)	0.0887 (8)	0.4641 (9)	0.4297 (7)	0.0902 (4)	0.4650 (4)	0.4304 (4)
Cl(1)	0.3047 (3)	0.1525 (3)	0.2246 (2)	0.3057 (1)	0.1540 (1)	0.2249 (1)
Cl(2)	0.1148 (2)	0.7206 (2)	0.0575 (2)	0.1151 (1)	0.7206 (1)	0.0586 (1)
O(1)	0.3946 (5)	0.1115 (5)	0.2906 (5)	0.3957 (3)	0.1111 (4)	0.2908 (3)
O(2)	0.2662 (11)	0.0978 (10)	0.1563 (9)	0.2691 (7)	0.1011 (7)	0.1557 (5)
O(3)	0.3273 (9)	0.2332 (10)	0.1986 (12)	0.3299 (5)	0.2364 (6)	0.2017 (7)
O(4)	0.2332 (8)	0.1693 (10)	0.2606 (7)	0.2349 (5)	0.1704 (6)	0.2617 (5)
O(5)	0.0832 (5)	0.6590 (5)	0.1184 (4)	0.0840 (3)	0.6581 (3)	0.1188 (3)
O(6)	0.1722 (5)	0.6687 (5)	0.0106 (5)	0.1729 (4)	0.6686 (3)	0.0126 (3)
O(7)	0.0229 (5)	0.7591 (5)	−0.0113 (5)	0.0237 (3)	0.7608 (3)	−0.0094 (3)
O(8)	0.1737 (5)	0.7983 (6)	0.1097 (5)	0.1756 (4)	0.7982 (3)	0.1108 (3)

ion and from 2.07 to 2.29 Å for the Zn(II) ion.

From the above discussion it appears that the molecular geometry of the $Zn((py)_3tach)^{2+}$ and $Co((py)_3tach)^{2+}$ ions are dominated by two factors. First, and foremost, the ligand forces the metal to adopt a trigonal-prismatic coordination, although steric interactions between H(C1), H(C7), and H(C13) reduce the symmetry from C_{3v} to C_3. Secondly, crystal packing causes distortion in the ion, which effectively eliminates all symmetry. For these reasons it is apparent that any discussion concerning "twist angles" is moot and dependent upon the approach[8] used to calculate them. The coordination sphere is probably best described as a trigonal prism, slightly tapered and twisted to account for steric interactions.

Structural studies[9-12] of Holm's clathro-chelates[13] have indicated that the average twist angles in these complexes varies according to Fe(II) > Co(II) ≈ Ni(II) ≈ Zn(II) ≈ 0. Although the position of Fe(II) in this series is in agreement with the simplest prediction from ligand field theory, it is clear that the strongly hindered PccBF ligand prevents a thorough comparison of the results with the theory. Consequently, structural studies of the $M((py)_3tach)^{2+}$ (M = Co, Ni, Zn) complexes take on added importance because the less hindered ligand allows the stereochemical preferences of the metal atoms to be clearly discerned. The observed variation, Ni(II) > Co(II) ≈ Zn(II), is exactly that predicted by the theory if allowance for the repulsions between electrons is included.

Experimental Section

Data were collected on a Picker FACS-1 diffractometer equipped with a Furnas monochromator (highly oriented graphite crystal, 002 plane, molybdenum source). A continuous θ–2θ scan was used for both crystals at a scan rate of 2.0°/min over a range of 2° in 2θ plus a dispersion correction for the $K\alpha_1$–$K\alpha_2$ splitting. Stationary-background counts of 20 s duration were recorded at each extreme of the scan. The source–monochromator–sample and sample–detector distances were 22.5 and 23.5 cm, respectively. The receiving aperture dimensions were 3 mm wide by 4 mm in height for the Zn crystal and 3 × 3.5 mm for the cobalt sample. A mechanical malfunction of the paper tape punch used to record the data rendered several hundred data in each set questionable. Since these data were randomly distributed, no attempt was made to recollect them, and they were rejected.

Precession photographs of both crystals indicated that they were monoclinic, space group $P2_1/c$, and were isomorphous. Cell dimensions and other crystallographic data are given in Table V. A total of 11 369 data, including redundancies, was collected for $4° \leq 2\theta \leq 55°$ and reduced to 5456 unique amplitudes for the $[Zn((py)_3tach](ClO_4)_2$ crystal, whose maximum dimension was 0.3 mm. The data reduction formula and other programs used have been described previously.[14]

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The structure was readily solved with direct methods and Fourier techniques. Since most hydrogen atoms were apparent in a difference Fourier synthesis, final refinement included hydrogen atoms placed in fixed idealized positions[6] (d(C–H) = 0.95 Å, B_{iso} = 4.0 Å^2). Full-matrix anisotropic refinement converged to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.042$ and $R_w(F) = \sum(w||F_o| - |F_c||)^2/\sum wF_o^2 = 0.053$. Weights, w, where calculated as $w(F_o) = \sigma(I)^{1/2}/2F_o$, where $\sigma(I)$ is based on counting statistics and an "ignorance factor" of 0.05. The goodness of fit for the last cycle was 1.22.

The [Co((py)$_3$tach)](ClO$_4$)$_2$ crystal used was an irregular shape with a maximum dimension of 0.25 mm. A total of 5235 reflections were measured for $4° \le 2\theta \le 45°$ and reduced as before to 2943 unique amplitudes. Refinement was identical with that of the Zn((py)$_3$tach)$^{2+}$ sample and converged to $R(F) = 0.079$ and $R_w(F) = 0.033$. The goodness of fit for the final cycle was 1.76.

Fractional coordinates for non-hydrogen atoms are given in Table VI.

Acknowledgment. The authors thank the Marshall H. Wrubel Computing Center for generous use of computing facilities.

Registry No. [Co((py)$_3$tach)](ClO$_4$)$_2$, 28849-62-9; [Zn((py)$_3$tach)](ClO$_4$)$_2$, 25765-80-4.

Supplementary Material Available: Complete lists of bonded distances and angles, hydrogen coordinates, anisotropic thermal parameters, and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514,
and Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute,
University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimer Bis(μ-methoxo)bis[bis(2,4-pentanedionato)chromium(III)], [(acac)$_2$Cr(OCH$_3$)]$_2$

HELEN R. FISCHER,[1a] JØRGEN GLERUP,[1b] DEREK J. HODGSON,*[1a] and ERIK PEDERSEN*[1b]

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The complex bis(μ-methoxo)bis[bis(2,4-pentanedionato)chromium(III)], [(acac)$_2$Cr(OCH$_3$)]$_2$, [CrC$_{11}$H$_{17}$O$_5$]$_2$, has been synthesized, and its crystal structure has been determined from three-dimensional counter X-ray data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two binuclear formula units in a cell of dimensions a = 10.958 (4) Å, b = 12.769 (3) Å, c = 10.073 (2) Å, α = 96.65 (2)°, β = 95.04 (2)°, and γ = 97.00 (2)°. Least-squares refinement based on 1960 independent data has led to a final value of the weighted R factor (on F) of 0.048. The complex consists of two chromium(III) ions which are bridged by two methoxy groups, the remaining sites in the roughly octahedral coordination sphere being occupied by the oxygen atoms of two cis bidentate 2,4-pentanedionato ligands. The average Cr–O(ligand) bond length is 1.965 (10) Å while the Cr–Cr separation is 3.028 (2) Å and the Cr–O–Cr bridging angles are 100.8 (2) and 101.2 (2)°. The average value of the dihedral angle between the O–C bonds on the bridging methoxo groups and the bridging Cr$_2$O$_2$ least-squares plane is 29.8°. The isomer studied here is the racemic isomer in contrast with the meso form of analogous dimers previously studied. The temperature dependence of the magnetic susceptibility of the complex has been fitted to a model assuming independent triplet, quintet, and septet energies. The fit is consistent with the Heisenberg model corrected for biquadratic exchange and yields a triplet-state energy of 9.83 (6) cm^{-1} above the ground-state singlet.

Introduction

In recent years we[2-9] and others[10-14] have been studying the influence on the magnetic properties of chromium(III) dimers of small structural changes, with particular emphasis on the impact of changes in the bridging geometry of μ-hydroxo and bis(μ-hydroxo) chromium(III) dimers. While the bridging Cr–O–Cr angle (ϕ) and the Cr–O bond length (R) were quickly seen to be significant, perhaps in analogy with earlier work on simpler systems,[15] it is only relatively recently that the frequently overriding importance of the dihedral angle (θ) between the O–H vector and the bridging Cr$_2$O$_2$ (or Cr$_2$O for μ-hydroxo complexes) plane has been recognized.[2-5,16,17] Regrettably, this parameter is often poorly determined even in precise X-ray structural studies because of the small contribution of hydrogen atoms to the X-ray structure factors.

While the use of neutron diffraction data provides, in principle, a solution to this problem, in practice a more valuable approach appears to be the synthesis and study of alkoxo-bridged rather than hydroxo-bridged complexes, since in the fomer the angle θ would be dependent only on chromium, oxygen, and carbon atomic parameters. The syntheses of several bis(μ-alkoxo) dimeric complexes of chromium(III) have been reported,[18-20] but unfortunately none of the three synthetic routes suggested has proved amenable to extension to large

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