

Figure 5. Sketch of Ni(CTH)MCl₄ complexes with the molecular reference frame.

orthogonality, reintroducing a nonzero antiferromagnetic component in the coupling, while strict orthogonality can be removed only if the symmetry requirement is removed, i.e. if the homology of the terms of the series is removed. A beautiful example of the first type of behavior is that of the bis(μ -hydroxo)-bridged copper(II) complexes,^{43,44} in which the coupling varies from ferro- to antiferromagnetic depending on the value of the Cu-O-Cu angle. The relative insensitivity of the strict orthogonality condition to the value of the bridging angle has been shown in the case of Cu-VO pairs^{5,24} and in the coupling between ground and excited states of copper(II) ions monitored by EPR spectra.⁴⁵

In order to decide whether the ferromagnetic coupling observed in the Ni-Cu pairs is determined by either strict or accidental degeneracy and which are the factors determining the large decrease in the ferromagnetic coupling when the cobalt(II) and manganese(II) derivatives are considered, a detailed analysis of the magnetic orbitals is now at order.

The magnetic orbitals in nickel(II) are xy and z^2 in the reference frame depicted in Figure 5. Since the dinuclear species has C_2 symmetry, these two orbitals can be classified within that point group as A and B respectively. The ground state for the compressed tetrahedron around copper is a linear combination of xy

and yz , both of B character. Therefore in the Ni-Cu pair two pathways are possible, the one involving the nickel(II) z^2 being weakly ferromagnetic. The pathway involving nickel(II) xy is expected to yield either ferro- or antiferromagnetic contribution, depending on the Ni-Cl-Cu angle. For angles close to 90° accidental orthogonality may occur, yielding ferromagnetic coupling. Therefore we suggest that the observed value of J is largely determined by the accidental orthogonality of the xy orbitals on nickel and copper.

The magnetic orbitals on cobalt correspond to the three t_2 orbitals of tetrahedral symmetry, therefore to the B combination of copper, so two others must be added, one of type B and the other of type A. Finally the five magnetic orbitals of manganese are obtained by adding to the three of cobalt two more of A symmetry. As far as symmetry is concerned, several strictly orthogonal ferromagnetic pathways are introduced (those involving an A orbital on one center and a B orbital on the other) together with others (those involving either A or B type orbitals on both centers) that can be either ferro- or antiferromagnetic depending on the Ni-Cl-M angle. The large decrease in the ferromagnetic coupling on passing from copper to cobalt and manganese shows that the antiferromagnetic contributions are taking over. This may be due to small angular variations in the series and to the fact that the condition of accidental orthogonality can be met for a pair of orbitals at an angle different from that of another pair.

It is therefore apparent that in the present series of complexes the accidental orthogonality or nonorthogonality of magnetic orbitals is determining the observed large variation in the magnetic properties. These results show how difficult it can be to elaborate strategies for obtaining strong ferromagnetic coupling based on accidental orthogonality of magnetic orbitals and how only the strict orthogonality relation yields a valuable way to synthesize compounds of which the ground state is the state of the highest spin multiplicity.

Registry No. Ni(CTH)ZnCl₄, 101224-31-1; Ni(CTH)CuCl₄, 101224-32-2; Ni(CTH)CoCl₄, 101224-33-3; Ni(CTH)MnCl₄, 101224-34-4.

Supplementary Material Available: Listings of hydrogen atom positional parameters (Table SI), anisotropic thermal parameters for non-hydrogen atoms (Table SII), and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Crystal Structure of (Azacaptene)cobalt(II) Diperchlorate and Strain Energy Minimization Analyses of the (Azacaptene)cobalt(III) and (Azacaptene)cobalt(II) Cations

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[Co^{II}(azacaptene)](ClO₄)₂, C₁₄H₃₀Cl₂CoN₄O₈S₃, crystallizes in the orthorhombic space group $Pna2_1$, with $a = 20.684(8)$ Å, $b = 12.820(5)$ Å, $c = 8.826(5)$ Å, and $Z = 4$. The complex cation is disordered with both enantiomers occupying the same site. The average Co(II)-N and Co(II)-S bond lengths are 2.08 and 2.31 Å, respectively. The cation adopts a lel_3 conformation, which molecular mechanics calculations suggest is the geometry of lowest strain energy. Molecular mechanics calculations also indicate that the relatively short Co(II)-N bond length is not a consequence of ligand constraints but is most likely due to the low-spin electronic state of the complex.

Introduction

The preparation and structure of a cobalt encapsulating macrobicyclic ligand with three nitrogen and three sulfur donors have been reported recently.¹ This ligand, 1-methyl-3,13,16-trithia-6,8,10,19-tetraazabicyclo[6.6.6]eicosane (azacaptene), like previously reported hexamine cryptates,^{2,3} so tightly binds the metal

that on reduction to Co(II) a stable nonlabile complex is obtained. Consequently, reactions of Co(III) and Co(II) azacaptene complexes can be studied in the absence of ligand-exchange processes.

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Table I. Crystal Data for [Co(azacapten)](ClO₄)₂

cryst syst	orthorhombic
space group	<i>Pna</i> 2 ₁
<i>a</i> , Å	20.684 (8)
<i>b</i> , Å	12.820 (5)
<i>c</i> , Å	8.826 (5)
<i>V</i> , Å ³	2340
<i>D</i> _{calcd} , g cm ⁻³	1.79 (2)
<i>D</i> _{obsd} , g cm ⁻³	1.724
empirical formula	C ₁₄ H ₃₀ Cl ₂ CoN ₄ O ₈ S ₃
<i>f</i> _w	608.4
<i>Z</i>	4
<i>F</i> (000), electrons	1260
abs coeff, cm ⁻¹	14.31
habit	prismatic
dimens, mm	0.20 × 0.20 × 0.30
transmission factors	0.83, 0.70
temp, K	294
diffractometer	STOE, two-circle, Weissenberg geometry
radiation	Mo Kα (λ = 0.71069 Å)
monochromator	graphite
mode	ω scan
2θ range, deg	1.5–55.0
no. of reflns measd	2450 (+ <i>h</i> , + <i>k</i> , + <i>l</i>)
no. of reflns used (<i>I</i> > 2.5σ(<i>I</i>))	1538

Also, crystallization of the Co(II) complex is facilitated.

Electron self-exchange between [Co^{II}(azacapten)]²⁺ and [Co^{III}(azacapten)]³⁺ has revealed an unusually large rate constant.⁴ It was suggested that this high rate constant is due to the Co(II) complex largely being in the low-spin state with relatively shorter Co(II)–X bond lengths that lead to a reduced reorganization energy.⁴

In order to establish whether the Co(II)–ligand donor atom bond lengths are indeed shorter than normal, we have determined the structure of [Co^{II}(azacapten)](ClO₄)₂. We also report a molecular mechanics study of [Co^{III}(azacapten)]³⁺ and [Co^{II}(azacapten)]²⁺ undertaken, in part, to establish whether the geometry about Co(II) can be ascribed to the low-spin magnetic state or to steric influences.

Experimental Section

[Co(azacapten)](ClO₄)₂ (50 mg) was dissolved in water (2 cm³) and the pH of the solution adjusted to 5 by addition of perchloric acid. Zinc dust (0.25 g) was added, and the container was sealed under nitrogen and shaken. After the mixture was allowed to stand overnight, deep purple crystals formed on the walls of the vessel. The solution and excess zinc were decanted under nitrogen and the crystals washed with ethanol containing 5% hydrochloric acid to remove adhering zinc. (Caution! Although the complexes reported here have given no indication of sensitivity to shock or grinding, perchlorate salts such as these are potentially dangerous and related materials have been known to detonate.)

Precession photographs of these crystals indicated the orthorhombic system while the conditions *k* + *l* = 2*n* for 0*kl* and *h* = 2*n* for *h*0*l* suggested the space groups *Pna*2₁ or *Pnam*. Cell constants at 21 °C were determined from ω(*h*00,0*k*0) and μ(00*l*) scans of axial reflections using a STOE Weissenberg diffractometer. Crystal data and data collection parameters are given in Table I. Data were collected with a crystal mounted about *c* and coated with epoxy resin to preclude aerial oxidation. Data were corrected for Lorentz, polarization, and absorption effects.⁵

Solution and Refinement of the Structure.⁵ Structure solution was initially attempted in the noncentrosymmetric space group *Pna*2₁, indicated by the presence of four molecules in the unit cell. The cobalt site was determined by analysis of a Patterson map, and the solution was confirmed by direct methods using MULTAN.⁶ Inclusion of the cobalt atom and calculation of a Fourier map revealed two coordination spheres, related to each other by reflection through the *z* = 0 plane. This imaging is expected for the space group *Pna*2₁; however, refinement of a connected

set of atoms did not lead to the disappearance of the imaged set as normally expected. The *E* value statistics calculated in the normalization routine of MULTAN⁶ were very close to those expected for a centrosymmetric space group, suggesting that either the space group is *Pnam*, with the complex ion disordered, since it does not have mirror symmetry that is crystallographically imposed in this space group, or the space group is *Pna*2₁, with the complex disordered so as to produce pseudocentrosymmetric statistics. To choose between the space groups, it was necessary to establish whether or not the two contributors to the disorder are exactly related by the mirror plane, a rather fine distinction. Refinement was continued in *Pna*2₁, and this was subsequently confirmed (vide infra) as the correct choice. The disorder corresponds to occupation of the site by each enantiomer of the complex as was observed in the structure of [Co(azacapten)](S₂O₆)_{1.5}·4H₂O,¹ though here all atoms of the CH₃C(CH₂)₂ cap are common to both enantiomers and there are separate contributors to the cysteamine ring atoms. The group multiplicity parameter defining the occupancy of the two sites refined to 0.584 (2). If the centrosymmetric space group had been the correct choice, then this value would have been expected to refine to exactly 0.5. Also, the disorder is not consistent with the centrosymmetric space group as some contributors to anion sites lacked images mirrored through the *z* = 0 plane.

All perchlorate groups were refined as rigid tetrahedral groups with fixed Cl–O bond lengths of 1.407 Å. Hydrogen atoms were included at sites calculated by assuming tetrahedral geometry about carbon (C–H = 0.97 Å). All parameters were refined by using full-matrix least squares. Individual interlayer scale factors were adjusted during the isotropic phase of refinement, which also employed unit weights. Only chlorine, sulfur, and cobalt atoms were refined with anisotropic thermal parameters, and hydrogen atoms were assigned a group isotropic thermal parameter. Refinement, minimizing $R_w = (\sum w^{1/2}(|F_o| - |F_c|)) / (\sum F_o)$ converged with *R* = 0.064, *R*_w = 0.067, and *w* = 1.76/(σ²(*F*_o) + 0.00087*F*_o²). The largest peaks of the last difference map are near one of the perchlorate anions, possibly indicating further disorder, but with heights less than 0.5 e Å⁻³ were considered too low for modeling.

Positional parameters are listed in Table II. The atom numbering in this table follows that used in ref 1. Thermal parameters and observed and calculated structure factors have been deposited. All scattering factors (Co(I) for Co(II)) and anomalous dispersion terms were taken from ref 7.

Molecular Mechanics Calculations

The Force Field. Metal complexes, mostly metal hexamines, have been modeled successfully by molecular mechanics (strain energy minimization) for a number of years now.^{8,9} We have recently developed a revised force field for such metal complexes that is significantly better than earlier force fields.^{10–14} Metal-centered valence angle distortions are replaced¹⁰ by 1,3-nonbonded repulsions between the donor atoms, reducing the number of functions involving the metal and donor atoms and facilitating the extension of the force field to enable modeling of metal complexes with more than one type of donor atom. We have previously reported the development of a force field for Co(II) hexamine complexes that successfully reproduced the structure of [Co^{II}(sepulchrate)]²⁺.¹⁴ Our aim here was to develop a force field for modeling Co(III) and Co(II) complexes with thioether ligands.

Bond length and valence angle deformation functions are represented by the harmonic approximation

$$E_x = \frac{1}{2}k(x - x_0)^2$$

Only two bond types involving sulfur have to be parametrized: cobalt to sulfur and carbon to sulfur. It has been established¹⁵ that the Co(III)–S bond is substantially weaker than the Co(III)–N bond. Therefore, a force constant half that for deformation of the latter was chosen while the zero was adjusted to give best fit to the crystallographically determined bond length and then checked by application to

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Table II. Atomic Positional Parameters ($\times 10^4$) for [Co(azacpten)](ClO₄)₂

atom ^a	x	y	z
Co	3619 (1)	2993 (1)	0
S(1)	3715 (4)	1410 (7)	1230 (10)
S(2)	4129 (4)	2247 (7)	-2031 (11)
S(3)	4620 (5)	3462 (7)	1007 (11)
N(1)	2707 (8)	2537 (12)	-896 (16)
N(2)	3529 (9)	4360 (13)	-836 (18)
N(3)	3072 (11)	3450 (16)	2231 (19)
N(4)	2434 (4)	4318 (7)	-164 (16)
C(1)	5576 (5)	710 (7)	-108 (19)
C(2)	4978 (4)	1441 (7)	-146 (16)
C(3)	4543 (6)	1046 (9)	1448 (14)
C(4)	4679 (6)	1298 (9)	-1451 (14)
C(5)	5228 (5)	2559 (8)	308 (14)
C(6)	3584 (13)	1858 (19)	3172 (21)
C(7)	3359 (12)	1544 (16)	-2658 (20)
C(8)	4800 (9)	4537 (14)	-432 (19)
C(9)	2931 (13)	2576 (17)	3017 (20)
C(10)	2787 (10)	2248 (14)	-2452 (19)
C(11)	4167 (8)	5141 (14)	-193 (21)
C(12)	2836 (12)	4874 (17)	-705 (22)
C(13)	2242 (9)	3485 (13)	-833 (19)
C(14)	2469 (10)	4016 (15)	1840 (20)
S(1')	1326 (5)	6462 (9)	3651 (11)
S(2')	934 (5)	7297 (10)	7123 (12)
S(3')	384 (6)	8502 (9)	3863 (12)
N(1')	2208 (14)	7679 (18)	5815 (22)
N(2')	1391 (12)	9496 (16)	5676 (20)
N(3')	1875 (11)	8467 (15)	3045 (19)
C(6')	1550 (11)	6853 (16)	1881 (21)
C(7')	1580 (14)	6427 (19)	7345 (23)
C(8')	334 (8)	9628 (13)	5277 (19)
C(9')	2071 (17)	7534 (20)	1844 (23)
C(10')	2151 (19)	7238 (22)	7451 (25)
C(11')	1011 (8)	10151 (14)	5309 (19)
C(12')	2039 (11)	10024 (16)	5464 (20)
C(13')	2798 (20)	8267 (24)	5590 (25)
C(14')	2438 (14)	9253 (18)	3436 (22)
Cl(1)	1601 (1)	327 (2)	1 (8)
O(1)	1371 (1)	844 (2)	1291 (8)
O(2)	1372 (1)	840 (2)	-1313 (8)
O(3)	2279 (1)	361 (2)	-36 (8)
O(4)	1380 (1)	-699 (2)	-218 (8)
O(1')	192 (1)	418 (2)	-1262 (8)
O(2')	1704 (1)	1242 (2)	838 (8)
O(3')	1280 (1)	-374 (2)	991 (8)
O(4')	2193 (1)	-116 (2)	-457 (8)
Cl(2)	1037 (1)	3180 (2)	4975 (9)
O(5)	1563 (1)	2491 (2)	4851 (9)
O(6)	444 (1)	2691 (2)	4696 (9)
O(7)	1139 (1)	3952 (2)	3838 (9)
O(8)	1034 (1)	3717 (2)	6369 (9)
O(5')	1271 (1)	2707 (2)	6297 (9)
O(6')	1149 (1)	2486 (2)	3756 (9)
O(7')	375 (1)	3397 (2)	5039 (9)
O(8')	1387 (1)	4100 (2)	4625 (9)
O(5'')	1567 (1)	2538 (2)	5307 (9)
O(6'')	1126 (1)	4206 (2)	5559 (9)
O(7'')	659 (1)	2734 (2)	6205 (9)
O(8'')	561 (1)	3212 (2)	3868 (9)

^a Primes indicate minor contributors to disordered molecules.

a second system.¹⁶ For the Co(II)-S bond, a still smaller force constant was chosen by analogy with the change observed in the cobalt to nitrogen force constant on going from Co(III) to Co(II), and the zero was again chosen to give the best fit. The force constant for the C-S bond was set 20% weaker than that for C-C as it is known that the former is weaker.¹⁷

The force constant and zero for the C-S-C valence angle were derived from those used by Allinger and Hickey.¹⁷ The force constant for Co-S-C deformation was taken from the value for Co-O-C¹⁸ while those for S-C-H and S-C-C were set at 75% of the N-C-H and N-C-C values. Zeros were adjusted to give best fit where necessary. In the modeling

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Table III. Force Constants for Cobalt Thioether Complexes

bond	k_{ij} , kJ mol ⁻¹ Å ⁻²	r_{ij} , Å	
Co(III)-S	482	2.080	
Co(II)-S	361	2.240	
C-S	2410	1.820	
valence angle	k_{ijk} , kJ mol ⁻¹ rad ⁻¹	θ_{ijk} , rad	
Co-S-C	30	1.672	
C-S-C	151	1.646	
S-C-C	211	1.881	
S-C-H	151	1.888	
torsion angle	v_{ij} , kJ mol ⁻¹		
S-C	0.60		
nonbonded interaction	$10^{-3}A$, kJ mol ⁻¹	B , Å	C , kJ mol ⁻¹ Å ⁶
S...S	1025	3.55	7116
S...C	1009	3.92	2982
S...N	896	4.02	2440
S...H	168	3.81	1211

of azacpten and sepulchrate complexes, the question arises as to how the trigonal nitrogen capping atoms should be treated. Both tetrahedral and planar geometries have been observed for trigonal nitrogen,^{19,20} and therefore the unstrained C-N_{cap}-C angle might be set at 109.4 or 120°. Rather than specify a possibly incorrect model for this atom, we adopted a force constant of zero. This model successfully reproduced the structures of the capping groups in both [Co^{III}(sepulchrate)]³⁺ and [Co^{II}(sepulchrate)]²⁺.¹⁴

Rotation about dihedral angles is restricted by functions of the form

$$E_{\phi} = \frac{1}{2}v_{ij}(1 + \cos 3\phi)$$

The only additional torsional function required is that describing rotation about the C-S bond. Coordinated thioether sulfur atoms have one lone pair of electrons and therefore might be considered as being approximately tetrahedral. Deformation about the C-S bond then, was treated the same as for other tetrahedral atoms, and a force constant 20% less than that for deformation about C-N was employed. Nonbonded interactions in this force field are described by Buckingham functions of the form

$$E_{nb} = A \exp(-Br_{ij}) - C/r_{ij}^6$$

The van der Waals radius of sulfur is 1.85 Å,²¹ and therefore, by comparison with nonbonded interaction functions employed for other atoms, the minimum for the sulfur to sulfur interaction should fall between 3.90 and 4.00 Å.⁸ A suitable function then was derived from that for chlorine ($d_{\min} = 3.87$ Å)²² by minor adjustment of the parameters A , B , and C . Parameters for the interactions between sulfur and other atoms were derived by taking geometric means of the equivalent parameters for sulfur to sulfur and atom to atom functions.

A list of the force constants specific to the cobalt thioether complexes is given in Table III. All other force constants used have been reported previously.^{10,14}

This force field has also been tested by application to *u-fac*-[Co(daes)₂]³⁺ (daes is (NH₂CH₂CH₂)₂S) and successfully reproduces the geometry of the coordinated ligand in that complex.¹⁶

Energy Minimization. The total strain energy is obtained by summing over the four interaction types over all interactions:

$$U_{\text{total}} = \sum E_b + \sum E_{nb} + \sum E_{\phi} + \sum E_{\psi}$$

U_{total} was minimized by variation of all independent Cartesian coordinates using the Newton-Raphson technique reported by Boyd.²³ All geometries were refined until shifts were less than 0.001 Å.

Results

Description of the Structure. The structure is held together by hydrogen bonds between all amino hydrogen atoms and the

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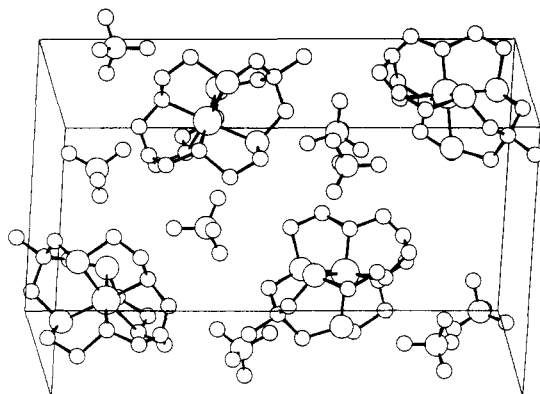


Figure 1. View of the unit cell of $[\text{Co}(\text{azacapten})](\text{ClO}_4)_2$. Lesser contributors to the disorder are omitted for clarity.

perchlorate anions. Similar interactions are observed between each contributor to the disorder of the complex and the anions. A view of the unit cell, with minor contributors to the disorder removed for clarity, is shown in Figure 1.

The structure confirms that the complex is $[\text{Co}(\text{azacapten})]^{2+}$ with the same atomic connectivity as that observed for the Co(III) species.¹ The gross geometry of the complex is also similar to that observed in the two Co(III) azacapten structures¹ with each cysteamine chelate ring adopting a conformation (*lel*) with the C–C vector parallel to the C_3 axis of the complex. Bond lengths to atoms that lie on the C_3 axis vary widely, suggesting that these atoms actually occupy two adjacent sites, whereas in modeling the disorder it was necessary to assume only one site. In order to obtain meaningful values for the geometrical parameters, they were averaged by assuming C_3 symmetry and over the two contributors to the disorder with the contributors weighted according to their refined occupancy. The values obtained for C–C, S–C, and N–C bond lengths are very close to those observed in the Co(III) azacapten complexes, suggesting that this averaging was a reasonable approach.

The Co–S bond length at 2.313 Å is longer than that found for the Co(III)–S bond (2.226 (1) Å)¹ and is comparable with the average value of 2.341 Å (range 2.251 (1)–2.479 (1) Å) found in $[\text{Co}^{\text{II}}(\text{hexathio-18-crown-6})]^{2+}$.²⁴ The Co–N bond length of 2.076 Å is shorter than that found in the high-spin hexamine cryptate $[\text{Co}^{\text{II}}(\text{sepulchrates})]^{2+}$ complex (2.164 Å).³ $[\text{Co}(\text{azacapten})]^{2+}$ is reported to be low-spin, and it seems probable that the shorter Co–N distance here is a consequence of the electronic properties. Short N–C bonds in the $\text{N}(\text{CH}_2)_3$ cap, as found here, have been observed in all other structures where these capping groups are present.^{1–3} Average bond lengths and valence angles are given later in Table VI, where they are compared to the energy-minimized values.

Analogy with the hexamine cryptate cobalt complex, $[\text{Co}(\text{sepulchrates})]^{2+}$,^{2,14} would suggest that conformational isomerism in $[\text{Co}(\text{azacapten})]^{2+}$ might arise from both the orientation of the caps relative to the rest of the complex and the orientation of the C–C vectors of the cysteamine rings relative to the C_3 axis of the complex. However, Dreiding models indicate that the capping groups of azacapten are substantially more rigid than those of sepulchrates and their relative orientations are fixed. Therefore, only the conformations of the cysteamine rings need to be considered. Initially, only those conformers with potential C_3 symmetry, *lel*₃ and *ob*₃, were considered, where *lel* and *ob* indicate the conformers in which the C–C vector is parallel to and at an angle to the C_3 axis of the complex.

Starting coordinates for *lel*₃- $[\text{Co}(\text{azacapten})]^{3+}$ were derived from the crystal structure coordinates while those for the *ob*₃ conformer were derived by using the molecule-building program CART.²⁵ Refinement to true potential energy minima in each case

Table IV. Minimized Strain Energies (kJ mol^{-1}) for the Conformers of $[\text{Co}(\text{azacapten})]^{2+}$

conformer	E_b	E_{nb}	E_θ	E_ϕ	U_{total}
(a) $[\text{Co}(\text{azacapten})]^{3+}$					
<i>lel</i> ₃	31.7	66.6	27.5	36.0	161.8
<i>ob</i> ₃	40.1	115.1	134.9	38.0	328.1
diff	8.4	48.5	107.4	2.0	166.3
(b) $[\text{Co}(\text{azacapten})]^{2+}$					
<i>lel</i> ₃	8.4	29.1	27.6	39.1	104.2
<i>ob</i> ₃	13.1	67.0	142.1	41.8	264.0
diff	4.7	37.9	114.5	2.7	159.8

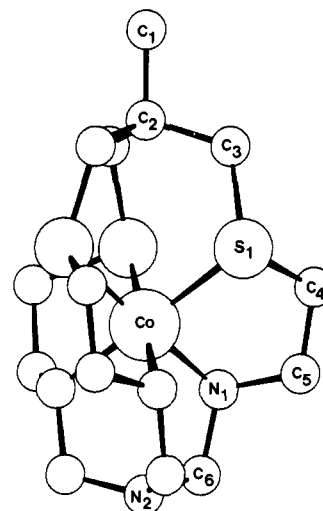


Figure 2. Plot of the energy-minimized geometry for *lel*₃- $[\text{Co}(\text{azacapten})]^{3+}$ with atom-numbering scheme used in Tables V and VI.

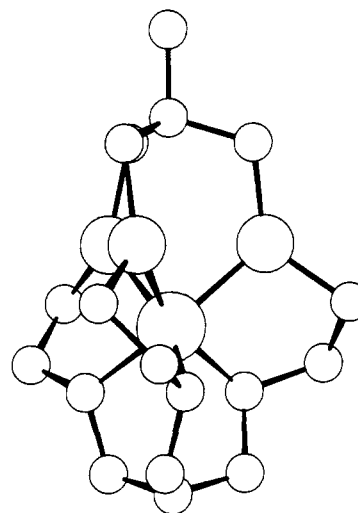


Figure 3. Plot of the energy-minimized geometry for *ob*₃- $[\text{Co}(\text{azacapten})]^{3+}$.

led to geometries with strictly maintained C_3 symmetry. These energy-minimized coordinates were used as the starting point for the Co(II) conformers. Again, refinement to potential energy minima resulted in geometries possessing C_3 symmetry. Final strain energies for all refined geometries are listed in Table IV.

A very large preference for the *lel*₃ conformer over the *ob*₃ conformer is found for both Co(III) and Co(II). For this reason it was felt that the lower symmetry (*lel*₂*ob* and *ob*₂*lel*) conformers did not warrant study. The higher strain energy of the *ob*₃ conformer arises mostly from increased valence angle terms. The largest contributor is the C–S–C angle, which in the Co(III) case is opened to 130.5°, corresponding to a strain energy of 30 kJ mol^{-1} . This distortion apparently arises because the rigidity of the $\text{CH}_3\text{C}(\text{CH}_2)_3$ cap restricts the radial expansion of the ligand,

(24) Hartman, J. R.; Hints, E. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1984**, 386.

(25) Hildebrandt, R. L. *J. Chem. Phys.* **1969**, *51*, 1654.

Table V. Comparison of Solid-State and Energy-Minimized Structural Parameters for lel_3 -[Co(azacpten)]³⁺

	crystal structure	energy minimized
Bond Lengths, Å		
Co-S(1)	2.226 (1)	2.240
Co-N(1)	2.009 (3)	1.982
C(1)-C(2)	1.544 (10)	1.546
C(2)-C(3)	1.529 (4)	1.549
S(1)-C(3)	1.814 (4)	1.826
S(1)-C(4)	1.819 (4)	1.819
N(2)-C(6)	1.438 (5)	1.445
Valence Angles, deg		
S(1)-Co-N(1)	88.0 (1)	88.6
S(1)-Co-S(1')	91.2 (1)	89.4
N(1)-Co-N(1')	91.3 (1)	90.2
Co-S(1)-C(3)	111.1 (1)	112.5
Co-S(1)-C(4)	97.2 (2)	97.1
Co-N(1)-C(5)	111.0 (3)	111.2
Co-N(1)-C(6)	113.9 (2)	114.1
C(1)-C(2)-C(3)	106.5 (3)	106.9
C(3)-C(2)-C(3')	112.3 (3)	111.9
C(2)-C(3)-S(1)	116.5 (3)	114.8
C(3)-S(1)-C(4)	104.7 (2)	104.3
S(1)-C(4)-C(5)	104.5 (3)	105.5
C(4)-C(5)-N(1)	110.1 (3)	109.7
C(5)-N(1)-C(6)	112.0 (3)	112.0
N(1)-C(6)-N(2)	113.1 (3)	111.9
C(6)-N(2)-C(6')	114.7 (2)	114.7
Torsion Angles, deg		
Co-S(1)-C(3)-C(2)	22.1 (3)	28.0
Co-S(1)-C(4)-C(5)	-42.7 (3)	-39.8
Co-N(1)-C(5)-C(4)	-47.5 (4)	-47.8
Co-N(1)-C(6)-N(2)	-10.4 (5)	-14.1
S(1)-C(3)-C(2)-C(1)	166.2 (3)	163.1
S(1)-C(3)-C(2)-C(3')	-77.5 (4)	-80.1
S(1)-C(3)-C(2)-C(3'')	50.0 (4)	46.4
S(1)-C(4)-C(5)-N(1)	60.6 (4)	58.5
N(1)-C(6)-N(2)-C(6')	74.6 (5)	76.9
N(1)-C(6)-N(2)-C(6'')	-61.3 (5)	-59.1
N(2)-C(6)-N(1)-C(5)	116.0 (4)	113.4
C(2)-C(3)-S(1)-C(4)	126.1 (3)	132.0
C(3)-S(1)-C(4)-C(5)	-156.7 (3)	-155.2
C(4)-C(5)-N(1)-C(6)	-175.4 (4)	-176.8

which is necessary on going from lel_3 to ob_3 .

Views of the energy-minimized lel_3 and ob_3 conformers are shown in Figures 2 and 3, respectively. Comparisons of the detailed geometry observed in the solid state with those of the energy-minimized lel_3 conformers of [Co(azacpten)]³⁺ and [Co(azacpten)]²⁺ are given in Tables V and VI, respectively.

Discussion

The minimized strain energies suggest that for both [Co^{III}(azacpten)]³⁺ and [Co^{II}(azacpten)]²⁺ only the lel_3 geometry will be observed. This is in accord with the observation of the lel_3 geometry in the two crystal structures of the Co(III) complex¹ and in the structure reported here. The ¹H and ¹³C NMR spectra of both the Co(III) and Co(II) complexes indicate C₃ symmetry,

Table VI. Comparison of the Solid-State and Energy-Minimized Structural Parameters for [Co(azacpten)]²⁺

	crystal structure	energy minimized
Bond Lengths, Å		
Co-S(1)	2.313	2.307
Co-N(1)	2.076	2.164
C(1)-C(2)	1.554	1.548
C(2)-C(3)	1.547	1.551
S(1)-C(3)	1.904	1.828
S(1)-C(4)	1.826	1.824
N(2)-C(6)	1.438	1.449
Valence Angles, deg		
S(1)-Co-N(1)	86.0	87.5
S(1)-Co-S(1')	90.4	91.4
N(1)-Co-N(1')	90.1	91.0
Co-S(1)-C(3)	106.2	107.8
Co-S(1)-C(5)	95.1	95.8
Co-N(1)-C(5)	112.6	107.7
Co-N(1)-C(6)	113.9	110.5
C(1)-C(2)-C(3)	105.7	106.6
C(3)-C(2)-C(3')	112.8	112.2
C(2)-C(3)-S(1)	111.1	116.3
C(3)-S(1)-C(4)	97.2	104.9
S(1)-C(4)-C(5)	104.5	108.4
C(4)-C(5)-N(1)	107.7	109.9
C(5)-N(1)-C(6)	110.7	114.2
N(1)-C(6)-N(2)	112.5	112.5
C(6)-N(2)-C(6')	115.4	117.5

consistent with the molecular mechanics predictions but equally consistent with a rapid interchange of conformations.

The geometry of [Co^{III}(azacpten)]³⁺, as observed in the solid state, is well reproduced by the force field described above, suggesting it is a reasonable model. Energy minimization of [Co^{II}(azacpten)]²⁺ performed by using the Co(II)-N bond length deformation parameters employed previously¹⁴ predicts a Co-N bond length of 2.16 Å. This is significantly longer than the observed value of 2.08 Å, suggesting that the short experimental value is not a consequence of strain-induced deformation. It is likely, therefore, that the relatively short Co-N bond length is a consequence of the complex largely being in the low-spin electronic state. The Co(III) and Co(II) structures show that on going from Co(III) to Co(II) an increase of 0.07 Å occurs in both Co-N and Co-S bond distances. This is substantially less than for [Co(sepulchrate)]^{2+,3+} complexes where an increase of 0.17 Å occurs. The smaller change for [Co(azacpten)]^{2+,3+} would lead to a much smaller Franck-Condon contribution to the barrier to electron transfer and so almost certainly contributes to the unusually rapid electron-exchange rate observed.⁴

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Registry No. [Co^{II}(azacpten)](ClO₄)₂, 101031-49-6.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters and a figure showing the atom-numbering scheme (12 pages). Ordering information is given on any current masthead page.