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 (32) After this paper was submitted an article appeared³³ reporting the formation of a μ_3 -oxo derivative of uranium(IV). The x-ray investigation has shown the presence of oxygen bridging two uranium and one lithium atoms.
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Notes

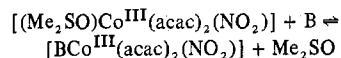
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Structure of Bis(acetylacetonato)(nitro)(2-aminopyrimidine)cobalt(III)

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Relatively few pyrimidine complexes have been studied crystallographically.¹ Substituted pyrimidines are typically expected to form less stable complexes than those formed by purines.² We recently reported³ an extensive series of stability constant data (in Me_2SO) for the reaction



where B = a number of purine and pyrimidine derivatives and acac = acetylacetonate. The purine complexes were typically more stable than the pyrimidine complexes, and we were successful in obtaining the structure of the bis(acetylacetonato)(nitro)(deoxyadenosine)cobalt(III) complex.³ The absence of any crystallographic data on a cobalt(III)-pyrimidine complex prompted us to pursue the preparation and crystallographic investigation of the title complex.

Experimental Section

The combination of aqueous solutions of 2-aminopyrimidine (0.5 mmol) and $\text{Na}[\text{Co}(\text{acac})_2(\text{NO}_2)_2]^{4-}$ (0.5 mmol) afforded a brown precipitate which was filtered and air-dried. The crystals, obtained by recrystallizing this product from a 1:1:1 by volume mixture of $\text{C}_3\text{H}_7\text{OH}-\text{THF}-\text{H}_2\text{O}$, belong to the monoclinic system, space group $P2_1$ or $P2_1/m$, with $a = 8.769$ (4) Å, $b = 13.899$ (7) Å, $c = 7.238$ (4) Å, $\beta = 94.39$ (4)°, $V = 879.6$ Å³, $D_{\text{measd}} = 1.48$ (1) g cm⁻³, and $D_{\text{calcd}} = 1.50$ g cm⁻³ for two molecules of $\text{C}_{14}\text{H}_{19}\text{N}_4\text{O}_6\text{Co}$ per unit cell.

All of several crystals, examined by both photographic and diffractometer methods, showed split peaks. These results plus our subsequent analysis (vide infra) indicate that a twin plane exists parallel to (010). For data collection we chose what we considered our best crystal, although it clearly had split peaks and marginal scattering power. A total of 4469 reflections (the $+h$ -hemisphere to 55° in 2θ (Mo $K\alpha$), graphite-monochromatized radiation) were surveyed on a Syntex PI automated diffractometer; of these, 2605 had $I > \sigma(I)$ and were subsequently employed. The data were corrected for Lorentz, polarization, and absorption effects. The crystal was a plate with perpendicular distances between faces as follows: (001)-(00 $\bar{1}$) 0.07 mm, (110)-(1 $\bar{1}$ 0) 0.21 mm, (1 $\bar{1}$ 0)-(110) 0.21 mm. The calculated transmission factors ranged from 0.80 to 0.93 (μ (Mo $K\alpha$) = 10.38 cm⁻¹). The corrected data were then symmetry averaged ($R = 0.053$) to yield a final set of 1462 independent data. Observational variances were based on counting statistics plus a term $(0.04I)^2$. An approximate absolute scale was determined by the method of Wilson.⁵

The complete structure was deduced from a three-dimensional Patterson synthesis. Refinement was initiated in the space group $P2_1/m$ which requires that the complex has mirror symmetry with the mirror plane populated by Co, the NO_2 group, and the 2-aminopyrimidine ring. Four cycles of isotropic refinement, minimizing

the quantity $\sum w(|F_o| - |F_c|)^2$, plus two cycles of anisotropic refinement reduced the R value ($\sum ||F_o| - |F_c|| / \sum |F_o|$) to 0.16. It was then evident that several atoms (NO_2 group, acac methyl carbons, and the NH_2 nitrogen) had anomalously large B_{22} components. After pseudo-symmetry problems for the reduced-symmetry space group $P2_1$ proved insurmountable, we continued our refinement in $P2_1/m$ with the knowledge that the mirror plane is a consequence of twinning and not intrinsic to the molecule, although the complex has approximate mirror symmetry.

Likely positions for all of the hydrogen atoms in the structure were obtained via a difference Fourier synthesis. Three further cycles of anisotropic refinement, with the hydrogen atoms accounted for but not refined, produced convergence (all shift/error less than 0.7) and a final R value of 0.149. The final weighted R value $[(\sum w(|F_o| - |F_c|)^2) / \sum w|F_o|^2]^{1/2}$ and goodness-of-fit $[(\sum (|F_o| - |F_c|)^2) / (\text{NO} - \text{NV})]^{1/2}$, where $\text{NO} = 1462$ data and $\text{NV} = 130$ variables] were 0.102 and 2.6, respectively. A final difference Fourier map showed no features exceeding +0.7 or -0.6 e/Å³. Final positional and thermal parameters for the nonhydrogen atoms are given in Table I. The hydrogen atom parameters, selected intramolecular dimensions, and a final list of observed and calculated structure factors have been deposited. Scattering factor tables for the nonhydrogen atoms⁶ and the hydrogen atoms⁷ were taken from common sources.

Discussion

A stereoview of the bis(acetylacetonato)(nitro)(2-aminopyrimidine)cobalt(III) complex is shown in Figure 1, while the crystal packing is illustrated in the [010] projection of Figure 2. The cobalt(III) center is six-coordinate, with the two acac ligands occupying the four coordination sites in the equatorial plane and the N-bonded nitro group and the N(3)-bonded 2-aminopyrimidine ligand in axial positions. The geometrical parameters in the primary coordination sphere are presented in Table II. As in the deoxyadenosine³ and triacanthine⁸ complexes of this system, the exocyclic amino group (N(2)H₂) forms a bifurcated hydrogen bond to two of the oxygen atoms (O(10) and its mirror image) of the acac ligands (Figure 1 and Table II). This favorable interligand hydrogen bonding and the absence of any repulsive forces confirm our original interpretation³ of the relatively large (27 M⁻¹) formation constant for this pyrimidine complex. As is found in many metal-purine complexes which form interligand hydrogen bonds,^{9,10} the exterior angles at the coordinated N(3) atom are dissymmetric, with the exocyclic Co-N(3)-C(2) angle (126.3 (6)°) being some 6° larger than the Co-N(3)-C(4) angle (120.1 (7)°). This dissymmetry is presumably in response to the geometrical requirements of the formation of the interligand hydrogen bonding.^{9,10}

The required coplanarity of the nitro group and the 2-aminopyrimidine ligand is a consequence of twinning in the crystal. However, we note that the dihedral angle between the plane of the nitro group and the nine-atom framework of the deoxyadenosine ligand in its complex³ is only 5 (1)°, so that approximate coplanarity of these two ligands is not unexpected.

The parameters in the nitro group are anomalous, owing to the large thermal ellipsoids assumed by this group. The geometry found in the 2-aminopyrimidine ligand is reasonably

Table I. Nonhydrogen Atom Parameters

| Atom | x | y | z | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|-----------------|----------|-------------------|----------|----------------------|----------|----------|-------------------|----------|-------------------|
| Co ^a | 2654 (2) | 2500 ^b | 160 (2) | 162 (3) ^c | 72 (1) | 137 (3) | 0000 ^b | 36 (2) | 0000 ^b |
| O(4) | 88 (2) | 250 ^b | -303 (2) | 33 (3) | 35 (2) | 37 (4) | 000 ^b | -12 (3) | 000 ^b |
| O(5) | -35 (2) | 250 ^b | -100 (2) | 28 (3) | 42 (3) | 37 (4) | 000 ^b | -1 (3) | 000 ^b |
| O(8) | 351 (1) | 340 (1) | -136 (1) | 25 (1) | 6 (1) | 20 (1) | -1 (1) | 2 (1) | 0 (1) |
| O(10) | 175 (1) | 340 (1) | 166 (1) | 23 (2) | 16 (1) | 19 (1) | 7 (1) | 4 (1) | -2 (1) |
| N(1) | 606 (2) | 250 ^b | 492 (2) | 23 (3) | 12 (1) | 42 (4) | 000 ^b | -13 (3) | 000 ^b |
| N(2) | 355 (2) | 250 ^b | 468 (2) | 35 (4) | 29 (2) | 15 (3) | 000 ^b | -5 (3) | 000 ^b |
| N(3) | 460 (1) | 250 ^b | 184 (1) | 17 (2) | 7 (1) | 21 (2) | 000 ^b | 12 (2) | 000 ^b |
| N(4) | 87 (2) | 250 ^b | -151 (2) | 22 (3) | 16 (1) | 21 (3) | 000 ^b | 4 (3) | 000 ^b |
| C(2) | 470 (2) | 250 ^b | 377 (2) | 26 (4) | 7 (1) | 30 (4) | 000 ^b | 16 (3) | 000 ^b |
| C(4) | 593 (2) | 250 ^b | 114 (2) | 24 (3) | 5 (1) | 32 (4) | 000 ^b | -4 (3) | 000 ^b |
| C(5) | 728 (2) | 250 ^b | 219 (3) | 26 (4) | 7 (1) | 45 (5) | 000 ^b | 10 (4) | 000 ^b |
| C(6) | 728 (2) | 250 ^b | 405 (4) | 16 (3) | 11 (1) | 66 (8) | 000 ^b | -9 (5) | 000 ^b |
| C(7) | 394 (1) | 485 (1) | -276 (2) | 36 (3) | 8 (1) | 56 (4) | -9 (1) | -23 (3) | 10 (2) |
| C(8) | 330 (1) | 431 (1) | -130 (1) | 22 (2) | 6 (1) | 27 (3) | -1 (1) | -11 (2) | 3 (1) |
| C(9) | 245 (2) | 475 (1) | 10 (2) | 34 (3) | 6 (1) | 49 (4) | 7 (1) | -20 (3) | -10 (2) |
| C(10) | 182 (2) | 430 (1) | 146 (2) | 26 (3) | 15 (2) | 31 (3) | 10 (2) | -16 (3) | -6 (2) |
| C(11) | 110 (1) | 490 (1) | 284 (2) | 33 (3) | 29 (2) | 39 (4) | 18 (2) | -7 (3) | 23 (2) |

^a Co parameters $\times 10^4$; all other parameters $\times 10^3$. ^b Fixed by symmetry. ^c Anisotropic ellipsoid expression: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

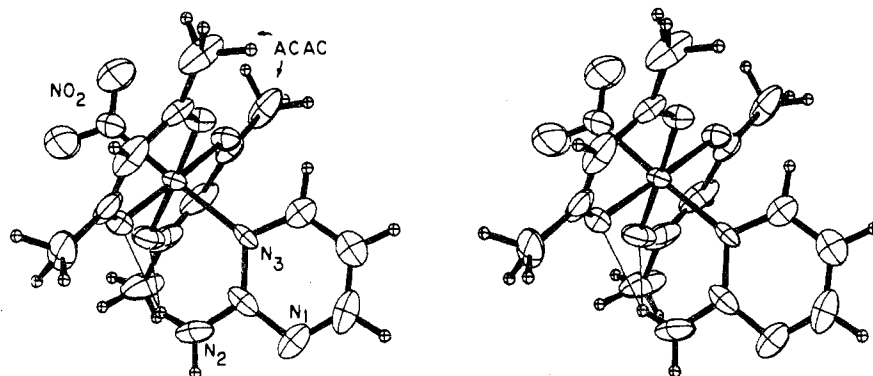


Figure 1. A stereoview of the bis(acetylacetonato)(nitro)(2-aminopyrimidine)cobalt(III) complex. The thermal ellipsoids are drawn at the 25% probability level.

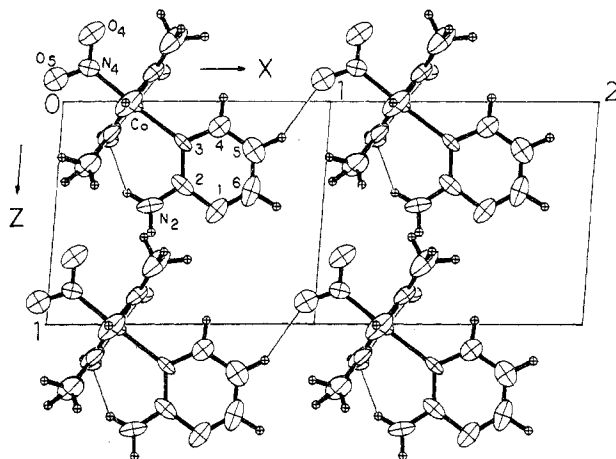


Figure 2. A projection of the unit-cell contents onto the (010) plane. Thin lines denote the intramolecular and intermolecular interactions of the type D-H...A described in the text and given in Table II. The labeled molecule has coordinates as given in Table I.

close to that found in the uncoordinated molecule.¹¹ The acac ligand geometry is similar to other observations.^{3,8}

The crystal packing, as illustrated in Figure 2, is dominated by interactions between the oxygen atoms of the nitro group, oxygen atom O(8) of the acac chelate, and the 2-aminopyrimidine ligand. Parameters in these interactions are included in Table II. The absence of strong interactions along the *b* axis, consisting of van der Waals-like contacts between the methyl groups of the acac ligands, probably underlies the

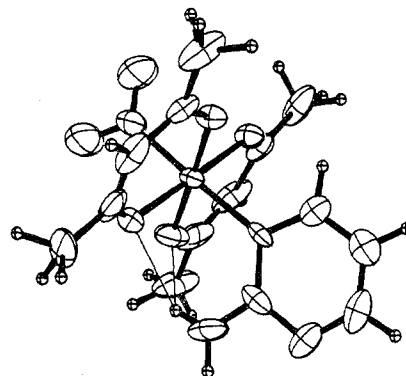


Table II. Selected Intra- and Intermolecular Distances (Å) and Angles (deg)

| (A) Primary Coordination Sphere about the Co | | | | | |
|--|-----------|-----------------------------|------------|-------|---------|
| Bond Lengths | | | | | |
| Co-O(8) | 1.865 (6) | Co-N(3) | 2.019 (7) | | |
| Co-O(10) | 1.874 (9) | Co-N(4) | 1.900 (10) | | |
| Bond Angles | | | | | |
| O(8)-Co-O(8) ^a | 84.6 (3) | O(8)-Co-N(4) | 88.4 (4) | | |
| O(8)-Co-O(10) | 95.6 (3) | O(10)-Co-O(10) ^a | 84.3 (3) | | |
| O(8)-Co-O(10) ^a | 178.7 (3) | O(10)-Co-N(3) | 91.4 (3) | | |
| O(8)-Co-N(3) | 89.8 (3) | O(10)-Co-N(4) | 90.3 (4) | | |
| | | N(4)-Co-N(3) | 177.6 (4) | | |
| (B) Interactions of the Type D-H...A | | | | | |
| D | H | A | D...A | H...A | D-H...A |

(1) Intramolecular
N(2) H(20) O(10) 2.88 (1) 2.26 128 (bifurcated)

(2) Intermolecular
N(2) H(21) O(8)^b 3.13 (1) 2.37 147
C(5) H(5) O(5)^c 3.23 (1) 2.33 150
N(2) H(21) O(4)^b 2.98 (1) 2.63 105
N(2) H(20) O(4)^b 2.98 (1) 2.68 102
C(6) H(6) O(4)^d 3.65 (1) 2.68 174

^a Symmetry transform: $x, 1/2 - y, z$. ^b Symmetry transform: $x, y, 1 + z$. ^c Symmetry transform: $1 + x, y, z$. ^d Symmetry transform: $1 + x, y, 1 + z$.

twinning problems we have encountered.

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Registry No. (2-Aminopyrimidine)Co^{III}(acac)₂(NO₂), 64457-12-1; Na[Co(acac)₂(NO₂)₂], 14024-47-6.

Supplementary Material Available: Hydrogen parameters, complete intramolecular dimensions, and a listing of structure factors (11 pages). Ordering information is given on any current masthead page.

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Structural Feature in TiCl₃, a Component in the Ziegler-Natta Catalyst, by X-Ray Absorption Studies

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The dependence of catalytic activity on the bonding and structure in catalysts has been proposed by several investigators.² The Ziegler-Natta type catalysts³⁻⁵ used in the polymerization of olefins continue to be an active field of investigation. Many questions relating to the constitution of these catalysts, the nature of the active sites, and the mechanism of their action remain to be resolved.⁶ Titanium trichloride, TiCl₃, is the typical solid component of the Ziegler-Natta type catalyst for stereospecific polymerization of α olefins; hence, a great interest in the knowledge of its crystal structure arises. Fiber-shaped (β form) and layered forms (α , γ , and σ) of TiCl₃ were studied using the powder x-ray technique.⁷ Optical microscopy⁸ linked polymerization at the surface of a TiCl₄-AlR₃ crystal face to localization of the active site, and single-crystal x-ray diffraction⁹ work with (C₂H₅)₂TiCl₂Al(C₂H₅)₂ confirmed the bimetallic nature of the catalyst. Despite these efforts, however, the Ti-Cl distance remains unknown.

We report the interatomic bond distance of TiCl₃ by the analysis of the extended x-ray absorption fine structure (EXAFS). This technique does not rely on single crystals and has been used previously to determine interatomic distances in iron-sulfur proteins,¹⁰ in copper salts in aqueous solutions,¹¹ and in polymer-bound rhodium(I) catalysts.¹²

Experimental Section

The photoabsorption K edge of Ti in TiCl₃ was measured using the tunable x-ray synchrotron source at the Stanford Synchrotron Radiation Project at Stanford University. The instrumentation has been previously described.¹³

The measurement of the intensity, I_0 , of the incident x-ray radiation passing through one ionization chamber (He + N₂) and the transmitted

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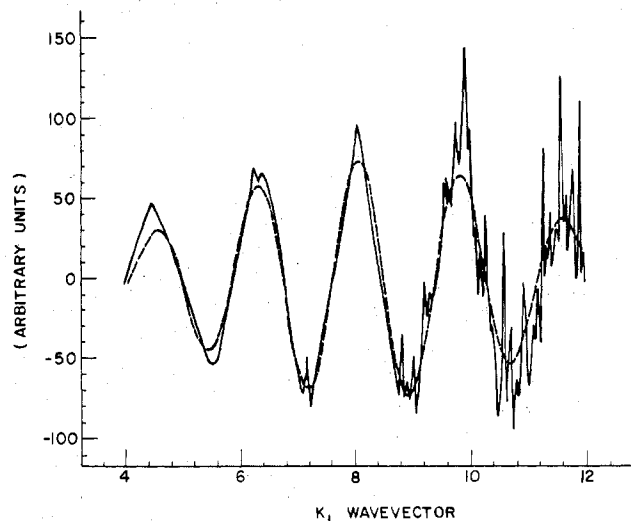


Figure 1. The Ti EXAFS of TiCl₃ where the raw data (—) and Fourier-filtered data (---) have had the background removed.

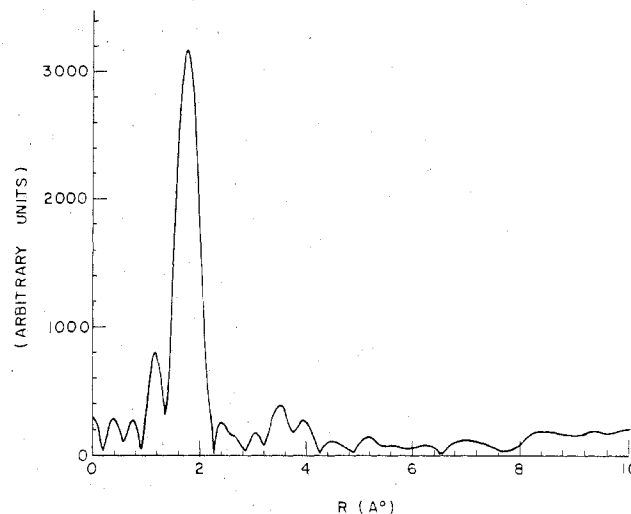


Figure 2. Fourier transform of the raw data.

intensity, I , through the sample and finally to a second ionization chamber (N₂) allows the relationship $\mu x = \ln(I_0/I)$, where μ is the linear absorption coefficient and x is the absorber thickness, to be plotted against the photon energy.

The data were taken on violet γ -TiCl₃ purchased from Alfa-Ventron. The sample was sealed between two thin layers of Kapton tape which is transparent to the x rays and protects the moisture- and air-sensitive TiCl₃ sample.

The current theoretical view of EXAFS^{15,16} is that the modulation of the x-ray absorption, $\chi = (\mu - \mu_0)/\mu_0$, is due to the interference between the backscattered and outgoing photoelectrons in the photoabsorption matrix element, where μ_0 is the absorption coefficient of an isolated atom. Thus, the modulation of $\Delta\mu/\mu$ of the x-ray absorption coefficient of an atom is given by eq 1, where N_j is the

$$\frac{\Delta\mu}{\mu} = \sum_j \frac{-N_j |f_j(k, \pi)| e^{-2\sigma_j^2 k^2}}{R_j^2 k} \sin(2kR_j + \phi_j(k)) \quad (1)$$

number of scattering atoms j at a distance R_j to the absorbing atom with a Debye-Waller like factor $e^{-2\sigma_j^2 k^2}$. The ϕ_j and f_j are energy-dependent phase shifts and amplitude functions for the scatterers, respectively, and k is the wavevector of the emitted photoelectron.

The raw data for TiCl₃ where Ti is the absorber is given in Figure 1, showing a single frequency, indicative of a single distance. The Fourier transform of the data is given in Figure 2.

Two methods were used to determine the Ti-Cl interatomic distance. One method¹⁷ used theoretical phase shifts, ϕ_j , and amplitudes, f_j , to fit the data to eq 1. An empirical method^{13a} with