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Transition-Metal Complexes of 1,9-Disubstituted Adenine Derivatives. Synthesis and Structure of [Bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)]-[bis(acetylacetonato)(dinitro)cobalt(III)]

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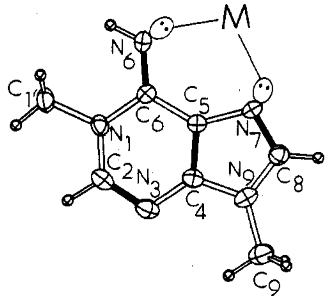
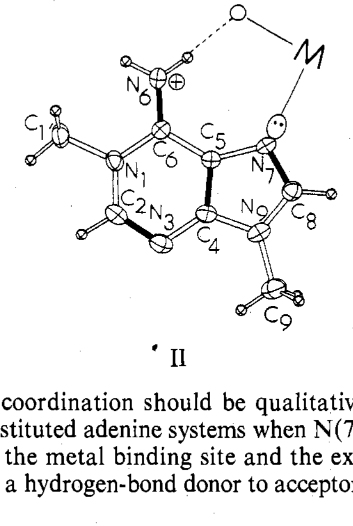
The synthesis and structure of the title complex are reported. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 9.848$ (3) Å, $b = 22.250$ (7) Å, $c = 8.501$ (2) Å, $\alpha = 94.98$ (2)°, $\beta = 93.69$ (2)°, $\gamma = 107.51$ (2)°, $V = 1761.7$ (9) Å^3, $Z = 2$, $d_{\text{measd}} = 1.56$ (1) g cm^{-3}, and $d_{\text{calcd}} = 1.54$ g cm^{-3}. Intensities for 4980 independent reflections were collected by counter methods on an automated diffractometer operating in the θ–2θ mode and employing Mo Kα monochromatized radiation. The structure was solved by standard heavy-atom Patterson methods. Full-matrix least-squares refinement has led to final R and weighted R values of 0.086 and 0.084, respectively. In the complex cation, the cobalt(III) atom is six-coordinate with two bidentate acetylacetonate ligands in equatorial positions and the N-bonded nitro group and the N(7)-bonded 1,9-dimethyladeninium cation occupying axial positions. The two independent and centrosymmetric complex anions are also six-coordinate and the two nitro ligands are trans. The complex cation in addition to the Co(III)–N(7) bond has an asymmetric, bifurcated hydrogen-bond system involving one of the exocyclic amino hydrogen atoms of the purine ligand and two of the coordinated oxygen atoms of the acetylacetonate ligands.

Introduction

In addition to the possible role that 1,9-disubstituted adenine derivatives such as 1-methyladenosine play in the conformational and functional properties of nucleic acids,[1-4] it appeared to us that such molecules could be very versatile in their metal coordination properties.[5] In their neutral, imino form (illustrated for 1,9-dimethyladenine in I), they are capable of acting either as bidentate chelating agents, employing the lone-pair density at the endocyclic site N(7) and the exocyclic imino group N(6)H, or in a monodentate mode with N(7) as the sole binding site and with the possible utilization of the imino proton as a hydrogen-bond donor. In the protonated form (II) of 1,9-disubstituted adenine derivatives, their coordination should be qualitatively similar to neutral 9-substituted adenine systems when N(7) is commonly employed as the metal binding site and the exocyclic amino group acts as a hydrogen-bond donor to acceptor sites on other ligands in the primary coordination sphere about the metal center (II).



I



II

Table I. Crystal Data for [Bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)][bis(acetylacetonato)-(dinitro)cobalt(III)]

$a = 9.848$ (3) Å	$[\mathrm{Co(C_{17}O_6N_6H_{24})][Co(C_{10}O_8N_2H_{14})]}$
$b = 22.250$ (7) Å	mol wt 816.51
$c = 8.501$ (2) Å	$D_m = 1.56$ (1) g cm^{-3}
$\alpha = 94.98$ (2)°	$D_c = 1.54$ g cm^{-3}
$\beta = 93.69$ (2)°	space group: $P\bar{1}$
$\gamma = 107.51$ (2)°	$\mu = 10.32$ cm^{-1}
$V = 1761.7$ (9) Å^3	λ(Mo K$\bar{\alpha}$) 0.710 69 Å

As a first example of the coordination chemistry of 1,9-disubstituted adenine derivatives, we report here on the preparation and structure of the complex formed from the reaction of the 1,9-dimethyladeninium cation (II) and Na[Co(acac)$_2$(NO$_2$)$_2$], where acac = acetylacetonate. As in the structures of the complexes formed with the neutral 6-aminopurine donors deoxyadenosine[5] and triacanthine [6-amino-3-(γ,γ-dimethylallyl)purine],[6] the 1,9-dimethyladeninium cation is bound to the metal through N(7) and one of the amino protons forms a bifurcated hydrogen-bond system with two of the equatorially bound oxygen atoms of the acac ligands.

Experimental Section

1,9-Dimethyladenine Hydrochloride. 1,9-Dimethyladenine hydriodide[7] (6 g) in H_2O (120 mL) was passed through a Dowex 1–X8 ion-exchange column (20 g of Cl resin). The product was collected on addition of acetone and was washed with acetone. It was recrystallized from ethanol/H_2O (8:2); yield 80%. Anal. Calcd for $C_7ClH_{10}NCl$: C, 42.1; H, 5.0. Found: C, 42.4; H, 5.0.

[Co(acac)$_2$(NO$_2$)(1,9-dimethyladeninium)][Co(acac)$_2$(NO$_2$)$_2$]. A solution of 1,9-dimethyladeninium chloride (200 mg in 5 mL of H_2O) was added to a solution of Na[Co(acac)$_2$(NO$_2$)$_2$][8] (400 mg in 30 mL of H_2O). After 5 min of stirring, the reaction solution was left overnight. The product which formed was collected, washed with ice water (10 mL) followed by methanol (60 mL) and ether (30 mL), and air-dried. This material was used in the crystallographic study.

Collection and Reduction of the X-ray Intensity Data. Preliminary oscillation and Weissenberg photographs showed the crystal system to be triclinic. Unit-cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles of 15 carefully centered reflections on a Syntex $P\bar{1}$ automated diffractometer. The crystal density, measured by neutral buoyancy methods in carbon tetrachloride and cyclohexane, indicated two [bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)](1+) cations and two [bis(acetylacetonato)(dinitro)cobalt(III)](1−) anions

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Table II. Final Nonhydrogen Atom Parameters ($\times 10^4$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co(1)	6274 (1)	2437 (1)	3169 (1)	C(17)	5038 (7)	2540 (3)	160 (8)
O(11)	6813 (5)	3242 (2)	4348 (5)	C(18)	4833 (8)	1906 (3)	−315 (8)
O(12)	6911 (5)	2032 (2)	4783 (5)	C(19)	4612 (8)	2949 (3)	−943 (8)
O(13)	5606 (4)	2826 (2)	1541 (5)	C(20)	4910 (10)	806 (3)	−11 (10)
O(14)	5742 (5)	1624 (2)	2051 (5)	Co(2)	0	0	0
O(15)	9184 (5)	2887 (3)	3265 (6)	O(21)	775 (5)	881 (2)	−28 (6)
O(16)	8178 (5)	2546 (3)	947 (6)	O(22)	−1251 (6)	49 (2)	1571 (5)
N(1)	2309 (6)	3382 (3)	4787 (7)	O(25)	2058 (9)	406 (3)	1630 (9)
N(3)	1319 (6)	2419 (3)	5912 (7)	O(26)	1898 (9)	444 (4)	2715 (8)
N(6)	4255 (6)	3583 (3)	3290 (7)	N(20)	1475 (8)	18 (3)	1662 (7)
N(7)	4330 (6)	2233 (2)	4056 (6)	C(21)	410 (8)	1297 (3)	855 (9)
N(9)	2589 (7)	1667 (3)	5336 (7)	C(22)	−1347 (8)	566 (4)	2259 (9)
N(10)	8105 (6)	2655 (3)	2358 (7)	C(23)	−579 (9)	1165 (3)	1948 (9)
C(1)	2141 (8)	4003 (3)	4559 (9)	C(24)	−2413 (11)	485 (4)	3505 (10)
C(2)	1363 (8)	2998 (4)	5650 (8)	C(25)	1156 (9)	1965 (3)	600 (10)
C(4)	2376 (7)	2250 (3)	5284 (8)	Co(3)	5000	5000	0
C(5)	3436 (7)	2593 (3)	4450 (7)	O(31)	3458 (5)	4287 (2)	313 (5)
C(6)	3398 (7)	3209 (3)	4141 (7)	O(32)	3831 (5)	5483 (2)	−654 (6)
C(8)	3748 (8)	1690 (3)	4588 (8)	O(35)	4327 (6)	4099 (2)	−2617 (6)
C(9)	1650 (9)	1131 (4)	6028 (9)	O(36)	5312 (7)	5033 (2)	−3242 (6)
C(11)	7382 (7)	3364 (4)	5777 (9)	N(30)	4935 (6)	4673 (3)	−2186 (7)
C(12)	7430 (8)	2280 (4)	6161 (8)	C(31)	2161 (7)	4204 (3)	−195 (8)
C(13)	7641 (8)	2917 (4)	6708 (8)	C(32)	2482 (7)	5267 (3)	−1030 (8)
C(14)	7844 (9)	1853 (4)	7227 (8)	C(33)	1657 (7)	4653 (3)	−844 (9)
C(15)	7727 (10)	4044 (4)	6431 (9)	C(34)	1789 (8)	5720 (4)	−1641 (10)
C(16)	5038 (7)	2540 (3)	160 (8)	C(35)	1158 (8)	3557 (3)	−27 (9)

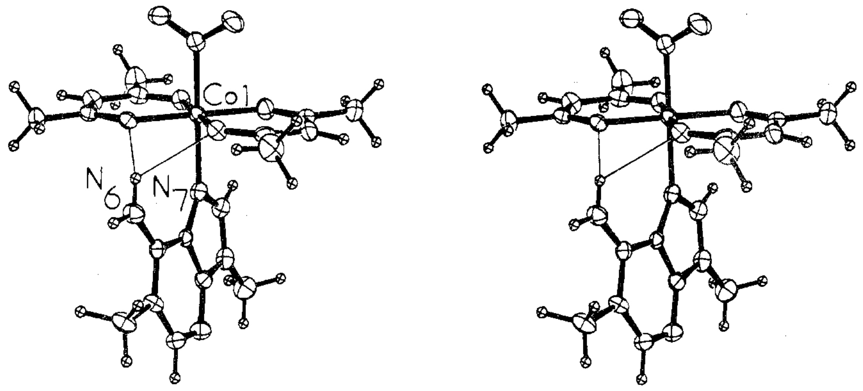

Figure 1. A stereoview of the molecular structure of the [bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)](1+) cation.

per unit cell. Complete crystal data are collected in Table I.

The intensities of 7072 reflections (including standards and a double set of 0*kl* reflections) in the $+h$ hemisphere to $2\theta = 55°$ were measured on the diffractometer, employing graphite-monochromatized Mo Kα radiation. The dark red platelike crystal used in data collection, mounted approximately along the *b* axis, had the following mean separations between principal faces: (100)–($\bar{1}$00) 0.10 mm, (001)–(00$\bar{1}$) 0.25 mm, and (010)–(0$\bar{1}$0) 0.35 mm. Intensity data were collected in the θ–2θ scan mode with individual scan speeds (2–24° min^{-1}) determined from a rapid scan at the calculated Bragg peak. The intensities of three standards were monitored after every 100 reflections and showed no systematic variation over the course of the experiment. The 7072 measured intensities were symmetry averaged and reduced to a set of 4980 intensities with $I \geq \sigma(I)$. Observational variances were assigned on the basis of the equation $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S, B_1, and B_2 are the scan and extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B = T_S/4$ for all reflections), and p was taken to be 0.04 and represents an estimate of the error proportional to the diffracted intensity.[9] The intensities and their standard deviations were corrected for Lorentz and polarization effects. An absorption correction was also applied based on the dimensions and face assignments given above and led to maximum and minimum transmission factors, F^2, of 0.90 and 0.76, respectively. An approximate absolute scale was determined by the method of Wilson.[10]

Solution and Refinement of the Structure. The positional coordinates of three independent cobalt atoms, one in a general position and two in special positions requiring $\bar{1}$ molecular symmetry, were deduced from a three-dimensional Patterson synthesis. A subsequent structure-factor Fourier calculation allowed the positioning of the remaining nonhydrogen atoms in the asymmetric unit. The cobalt atoms in special positions are associated with two independent [bis(acetylacetonato)(dinitro)cobalt(III)](1−) anions, while the [bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)](1+) cation has its cobalt atom in a general position. Four cycles of isotropic least-squares refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, led to an R value $[\sum ||F_o| - |F_c|| / \sum |F_o|]$ of 0.114. At this point, a difference-Fourier map was computed and positional assignments were obtained for the 38 hydrogen atoms. The isotropic thermal parameters of the hydrogen atoms were set about equal to the atom to which they were bonded. Three further cycles of refinement, employing anisotropic thermal parameters for the nonhydrogen atoms and holding the hydrogen-atom parameters fixed, led to convergence and a final R value of 0.086. The final weighted R value $[R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}]$ and goodness of fit $[(\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV}))^{1/2}$, where NO = 4980 observations and NV = 464 variables] were 0.084 and 2.2, respectively. A final difference-Fourier map had as its maximum feature a peak of 1.2 e/Å^3 near the cobalt atom, Co(3), of one of the dinitro anions.

Neutral scattering factor curves for the nonhydrogen and hydrogen[12] atoms were taken from standard sources. Anomalous dispersion corrections were applied to the scattering curves for all the nonhydrogen atoms.[13] Final positional parameters for the nonhydrogen atoms are collected in Table II. Anisotropic thermal parameters, parameters for the hydrogen atoms, best plane calculations, as well as a list of final calculated and observed structure factor amplitudes have been deposited. The crystallographic calculations were done with a standard set of computer programs.[14]

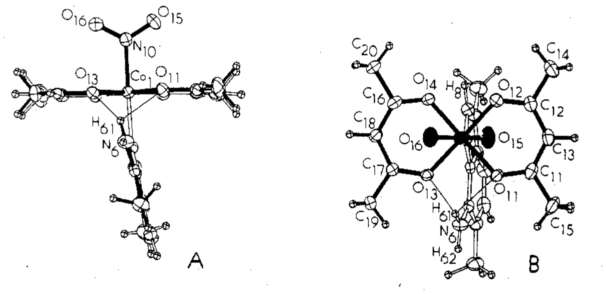

Figure 2. Two projection views of the [bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)](1+) cation: (A) a view parallel to the equatorial plane and along a line bisecting the two acac ligands; (B) a view parallel to the N(10)–Co(I) bond. In each view, thin lines denote the interligand, bifurcated hydrogen-bond system.

Results and Discussion

Description of the Molecular and Crystal Structure of [Bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III)][bis(acetylacetonato)(dinitro)cobalt(III)]. The molecular conformation of the [Co(acac)$_2$(NO$_2$)(1,9-dimethyladeninium)](1+) cation is presented in the stereoview of Figure 1. The complex cation is six-coordinate, with the two bidentate acac ligands occupying the four equatorial coordination sites [Co–O (average) = 1.880 (3) Å] and the N-bonded nitro group [Co–N distance = 1.912 (6) Å] and the N(7)-bonded 1,9-dimethyladeninium ligand [Co–N(7) = 2.040 (5) Å] in axial positions. The Co–N(7) bond length found here is about 0.04 Å longer than those observed in the deoxyadenosine [1.99 (3) Å][5] and the triacanthine [2.003 (4) Å][6] complexes we have reported earlier and may well result from the cationic nature of the 1,9-dimethyladeninium ligand. This lengthening of the Co–N(7) bond has no apparent effect on the *trans* Co–N(nitro) bond length as the value found here, 1.912 (6) Å, is nearly identical with the distance, 1.915 (4) Å, found in the tightly bound triacanthine complex.[6]

The overall conformational properties of the 1,9-dimethyladeninium complex are very similar to the deoxyadenosine and the triacanthine complexes.[5,6] The 1,9-dimethyladeninium plane is oriented about the Co–N(7) vector such that it approximately bisects the two equatorially bound acac ligands, Figures 1 and 2. In this orientation, the exocyclic amino group, N(6)H$_2$, on the purine ring forms a bifurcated hydrogen-bond system to two of the coordinated oxygen atoms of the acac groups, Figures 1 and 2. The parameters in these interligand hydrogen bonds are as follows: N(6)–H(61)···O(11), N(6)···O(11) = 2.95 (1) Å, H(61)···O(11) = 2.37 Å, angle N(6)–H(61)···O(11) = 123°; N(6)–H(61)···O(13), N(6)···O(13) = 2.83 (1) Å, H(61)···O(13) = 2.03 Å, angle N(6)–H(61)···O(13) = 150°. The asymmetry in the bifurcated, interligand hydrogen-bond system is markedly higher here than in any of the previous complexes of this type that we have examined. In part, at least, this asymmetry is induced by crystal packing forces (see below) which cause a significant tilting of the purine ring relative to the equatorial plane, Figure 2A.

Consistent with the formation of the interligand hydrogen-bond system,[15,16] the exocyclic bond angles at N(7) are highly dissymmetric, with the Co–N(7)–C(5) bond angle at 133.6 (4)° being about 12° larger than the Co–N(7)–C(8) bond angle at 121.5 (5)°. The magnitude of the dissymmetry in the exocyclic bond angles at N(7) observed here in the 1,9-dimethyladeninium complex is similar to that found in the deoxyadenosine (16°)[5] and the triacanthine (14°)[6] complexes and on the same order of magnitude we have observed in several other systems where interligand hydrogen bonding is found between exocyclic groups [6-amino or 6-oxo] on N(7)-bound purines and other ligands in the primary coordination sphere about a metal center such as Co(III) or Cu(II).[15,16] Furthermore, as in the deoxyadenosine[5] and triacanthine[6] complexes, the hydrogen atom off the imidazole carbon atom C(8) forms favorable contacts (2.68–2.71 Å) with the oxygen atoms [labeled O(12) and O(14), here] of the acac ligands which are not involved in the interligand hydrogen bonding. These C–H···O contacts may contribute slightly to the stability of the complex.

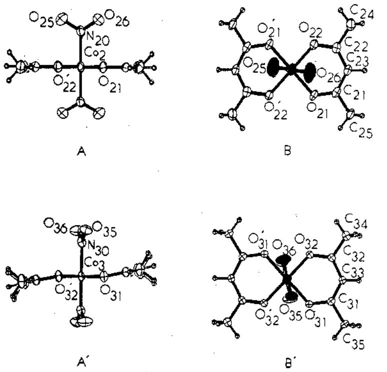

Figure 3. Projection views of the two independent [bis(acetylacetonato)(dinitro)cobalt(III)](1−) anions: (A, A′) views parallel to the equatorial plane and along a line bisecting the two acac ligands; (B, B′) views along the N(20)–Co(2) and N(30)–C(3) bonds, respectively.

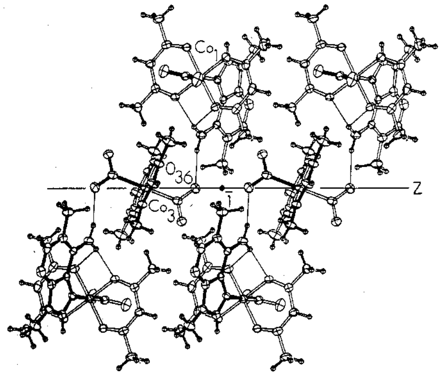

Figure 4. Interactions between the cationic 1,9-dimethyladeninium complex and one of the anionic dinitro complexes. Thin lines denote hydrogen bonds. The labeled crystallographic center of symmetry is at ($^1/_2$, $^1/_2$, 0).

One conformational feature which does not carry over from complex to complex is the relative orientation of the NO$_2$ ligand to the remainder of the system. In the deoxyadenosine[5] and 2-aminopyrimidine[17] complexes, the NO$_2$ plane and the purine or pyrimidine ligand are essentially coplanar, whereas in the triacanthine[6] and the 1,9-dimethyladeninium complexes, the dihedral angles between the NO$_2$ plane and the purine ring are 87.4 (5)° and 90.0 (7)°, respectively. The two orientations of the NO$_2$ plane in relationship to the acac ligand system seem sterically about equally favorable,[5,6] and crystal packing requirements probably lead to the observation of the different orientations in the various crystalline complexes.

There are several other conformational features of the [Co(acac)$_2$(NO$_2$)(1,9-dimethyladeninium)](1+) complex cation that are worthy of mention. The two acac ligands are individually quite planar and nearly parallel to each other with a dihedral angle of 1.7 (4)° between their mean planes. The two acac planes are not coplanar, however, with a mean distance of about 0.2 Å between their mean planes; the cobalt atom, Co(1), lies essentially midway between the two acac planes.

The nine-atom framework of the 1,9-dimethyladeninium ligand is moderately planar having a measurable fold of 2.6 (4)° about the C(4)–C(5) bond between the highly planar

Table III. Nonhydrogen Atom Interatomic Distances (Å) and Angles (deg)

(a) Primary Coordination Sphere about the Three Cobalt Atoms

Co(1)–O(11)	1.882 (4)	Co(1)–O(12)	1.879 (5)	Co(2)–O(21)	1.881 (5)	Co(3)–O(31)	1.889 (5)
Co(1)–O(13)	1.879 (4)	Co(1)–O(14)	1.876 (4)	Co(2)–O(22)	1.892 (5)	Co(3)–O(32)	1.886 (5)
Co(1)–N(10)	1.911 (6)	Co(1)–N(7)	2.040 (5)	Co(2)–N(20)	1.950 (7)	Co(3)–N(30)	1.926 (6)
O(11)–Co(1)–O(12)	95.2 (2)	O(12)–Co(1)–N(7)	89.1 (2)	N(7)–Co(1)–N(10)	178.2 (2)	O(31)–Co(3)–O(32)	94.8 (2)
O(11)–Co(1)–O(13)	85.8 (2)	O(12)–Co(1)–N(10)	91.6 (2)	O(21)–Co(2)–O(22)	95.7 (2)	O(31)–Co(3)–N(30)	90.4 (2)
O(11)–Co(1)–O(14)	178.3 (2)	O(13)–Co(1)–O(14)	95.9 (2)	O(21)–Co(2)–N(20)	90.3 (3)	O(32)–Co(3)–N(30)	88.6 (2)
O(11)–Co(1)–N(7)	89.2 (2)	O(13)–Co(1)–N(7)	90.3 (2)	O(22)–Co(2)–N(20)	89.4 (3)	O(31)–Co(3)–O(32)[b]	85.2 (2)
O(11)–Co(1)–N(10)	89.1 (2)	O(13)–Co(1)–N(10)	89.1 (2)	O(21)–Co(2)–O(22)[a]	84.3 (2)	O(31)–Co(3)–N(30)[b]	89.6 (2)
O(12)–Co(1)–O(13)	178.8 (2)	O(14)–Co(1)–N(7)	90.3 (2)	O(21)–Co(2)–N(20)[a]	89.7 (3)	O(32)–Co(3)–N(30)[b]	88.6 (2)
O(12)–Co(1)–O(14)	83.1 (2)	O(14)–Co(1)–N(10)	91.4 (2)	O(22)–Co(2)–N(20)[a]	90.6 (3)		

(b) Acetylacetonato Ligands

O(11)–C(11)	1.28 (1)	O(13)–C(17)	1.29 (1)	O(21)–C(21)	1.29 (1)	O(31)–C(31)	1.28 (1)
O(12)–C(12)	1.26 (1)	O(14)–C(16)	1.25 (1)	O(22)–C(22)	1.28 (1)	O(32)–C(32)	1.28 (1)
C(11)–C(13)	1.40 (1)	C(16)–C(18)	1.41 (1)	C(21)–C(23)	1.37 (1)	C(31)–C(33)	1.38 (1)
C(11)–C(15)	1.50 (1)	C(16)–C(20)	1.50 (1)	C(21)–C(25)	1.49 (1)	C(31)–C(35)	1.51 (1)
C(12)–C(13)	1.40 (1)	C(17)–C(18)	1.38 (1)	C(22)–C(23)	1.38 (1)	C(32)–C(33)	1.39 (1)
C(12)–C(14)	1.49 (1)	C(17)–C(19)	1.49 (1)	C(22)–C(24)	1.52 (1)	C(32)–C(34)	1.49 (1)
Co(1)–O(11)–C(11)	124.7 (5)	Co(1)–O(13)–C(17)	124.5 (4)	Co(2)–O(21)–C(21)	124.0 (5)	Co(3)–O(31)–C(31)	124.1 (4)
Co(1)–O(12)–C(12)	126.3 (5)	Co(1)–O(14)–C(16)	125.2 (5)	Co(2)–O(22)–C(22)	124.5 (5)	Co(3)–O(32)–C(32)	125.2 (4)
O(11)–C(11)–C(13)	125.0 (7)	O(14)–C(16)–C(18)	125.4 (7)	O(21)–C(21)–C(23)	125.5 (7)	O(31)–C(31)–C(33)	125.1 (6)
O(11)–C(11)–C(15)	114.0 (7)	O(14)–C(16)–C(20)	115.6 (7)	O(21)–C(21)–C(25)	114.1 (7)	O(31)–C(31)–C(35)	114.3 (6)
C(13)–C(11)–C(15)	121.7 (7)	C(18)–C(16)–C(20)	119.0 (7)	C(23)–C(21)–C(25)	120.4 (7)	C(33)–C(31)–C(35)	120.6 (6)
O(12)–C(12)–C(13)	124.0 (7)	O(13)–C(17)–C(18)	125.5 (7)	O(22)–C(22)–C(23)	125.1 (7)	O(32)–C(32)–C(33)	123.7 (7)
O(12)–C(12)–C(14)	115.8 (7)	O(13)–C(17)–C(19)	114.8 (6)	O(22)–C(22)–C(24)	114.9 (7)	O(32)–C(32)–C(34)	116.3 (6)
C(13)–C(12)–C(14)	120.2 (7)	C(18)–C(17)–C(19)	120.7 (7)	C(23)–C(22)–C(24)	120.0 (7)	C(33)–C(32)–C(34)	120.0 (7)
C(11)–C(13)–C(12)	124.6 (7)	C(16)–C(18)–C(17)	124.5 (7)	C(21)–C(23)–C(22)	125.2 (7)	C(31)–C(33)–C(32)	125.4 (7)

(c) Nitro Ligands

N(10)–O(15)	1.22 (1)	N(20)–O(25)	1.24 (1)	N(30)–O(35)	1.23 (1)
N(10)–O(16)	1.21 (1)	N(20)–O(26)	1.20 (1)	N(30)–O(36)	1.25 (1)
Co(1)–N(10)–O(15)	119.7 (5)	Co(2)–N(20)–O(25)	120.5 (6)	Co(3)–N(30)–O(35)	121.6 (5)
Co(1)–N(10)–O(16)	119.4 (5)	Co(2)–N(20)–O(26)	122.2 (6)	Co(3)–N(30)–O(36)	121.8 (5)
O(15)–N(10)–O(16)	120.9 (6)	O(25)–N(20)–O(26)	117.2 (7)	O(35)–N(30)–O(36)	116.6 (6)

(d) 1,9-Dimethyladeninium Ligand

N(1)–C(1)	1.47 (1)	C(5)–C(6)	1.43 (1)	N(3)–C(4)	1.33 (1)	C(8)–N(9)	1.33 (1)
N(1)–C(2)	1.36 (1)	C(5)–N(7)	1.39 (1)	C(4)–C(5)	1.37 (1)	N(9)–C(9)	1.47 (1)
N(1)–C(6)	1.37 (1)	C(6)–N(6)	1.30 (1)	C(4)–N(9)	1.38 (1)		
C(2)–N(3)	1.32 (1)	N(7)–C(8)	1.31 (1)				
C(1)–N(1)–C(2)	117.8 (6)	N(1)–C(6)–C(5)	114.0 (6)	N(3)–C(4)–N(9)	125.1 (6)	N(7)–C(8)–N(9)	113.9 (6)
C(1)–N(1)–C(6)	119.8 (6)	N(1)–C(6)–N(6)	120.5 (6)	C(5)–C(4)–N(9)	105.9 (6)	C(4)–N(9)–C(8)	106.5 (6)
C(2)–N(1)–C(6)	122.4 (6)	C(5)–C(6)–N(6)	125.5 (6)	C(4)–C(5)–C(6)	116.9 (6)	C(4)–N(9)–C(9)	124.9 (6)
N(1)–C(2)–N(3)	125.8 (7)	Co(1)–N(7)–C(5)	133.6 (4)	C(4)–C(5)–N(7)	109.3 (6)	C(8)–N(9)–C(9)	128.5 (6)
C(2)–N(3)–C(4)	111.7 (6)	Co(1)–N(7)–C(8)	121.5 (5)	C(6)–C(5)–N(7)	133.8 (6)		
N(3)–C(4)–C(5)	129.0 (7)	C(5)–N(7)–C(8)	104.4 (6)				

[a] Symmetry transformation $\bar{x}, \bar{y}, \bar{z}$. [b] Symmetry transformation $1-x, 1-y, \bar{z}$.

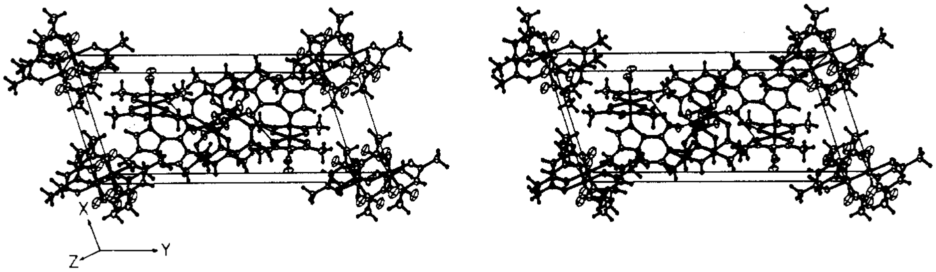

Figure 5. A stereoview of the unit-cell packing. Thin lines illustrate the intramolecular and intermolecular hydrogen bonding.

imidazole and pyrimidine rings. Such slight folding about the C(4)–C(5) bond is common to coordinated and uncoordinated purine ring systems.[18] As expected given the tilting of the 1,9-dimethyladeninium ligand relative to the equatorial plane, Figure 2A, Co(1) lies significantly out of the plane of the purine ligand (0.36 Å) and in a direction opposite to a slight, 0.1 Å, out-of-plane distortion of the exocyclic amino group.

The dimensions in the primary coordination sphere, those of the acac and nitro ligands, Table III, are consistent with other observations.[5,6,17] The molecular dimensions of the coordinated 1,9-dimethyladeninium cation are similar to those we have determined for the chloride salt,[19] with a slight elongation (~0.03 Å) of the bond lengths C(5)–C(6) and N(9)–C(4) and a contraction (~0.03 Å) in the N(9)–C(8) bond. The only major bond angle changes are an expansion of the C(6)–C(5)–N(7) angle by ~4° and a compensating shrinkage of the C(6)–C(5)–C(4) angle by ~3°.

Illustrations of the two independent $[Co(acac)_2(NO_2)_2]^-$ complex anions are presented in Figure 3. Each of these complex anions are required by crystallographic considerations to have at least $\bar{1}$ molecular symmetry. The dinitro anion containing Co(2), Figure 3A,B, is highly symmetric with Co(2)–O(acac) bond lengths of 1.889 (4) and 1.886 (5) Å and a Co(2)–N(nitro) bond length of 1.926 (6) Å which are essentially equivalent to those found in the 1,9-dimethyladeninium complex anion. The two acac ligands are planar and parallel (by symmetry) with only a slight stepping of 0.03 Å between their mean planes. The nitro group approximately bisects the two chelate rings of the acac ligands, Figure 3B, as was also observed in the complex cation, Figure 2B.

The dinitro anion containing Co(3), Figure 3A′,B′, is considerably less symmetric than that containing Co(2). The Co(3)–O(acac) distances of 1.881 (5) and 1.892 (5) Å are normal, but the Co(3)–N(nitro) bond length at 1.950 (7) Å is probably significantly longer than those found in the 1,9-dimethyladeninium complex cation and the dinitro anion containing Co(2). More dramatically, the two planar and parallel (by symmetry) acac ligands are markedly stepped by 0.5 Å, apparently owing to packing effects (see below). Also the nitro group approximately bisects the two acac ligands, Figure 3B′, as opposed to lying over the chelate rings as in the other two complex species. This latter observation seems to lend credence to the notion that the two different orientations of the NO_2 group relative to the acac system are about equally favorable (see above) and the orientation is susceptible to packing considerations. The molecular dimensions in the two independent dinitro anions are collected in Table III and are consistent with expectations.

The major features of the crystal packing are illustrated in Figures 4 and 5. Besides being involved in the bifurcated, interligand hydrogen bonding system described above, the exocyclic amino group of the N(7)-bound 1,9-dimethyladeninium cation also forms a strong intercomplex hydrogen bond to one of the oxygen atoms, O(36), of the dinitro complex about Co(3), Figure 4. The parameters in this intercomplex hydrogen bond are as follows: N(6)–H(62)···O(36) $(1-x, 1-y, -z)$, N(6)···O(6) = 2.98 (1) Å, H(62)···O(36) = 2.16 Å, angle N(6)–H(62)···O(36) = 155°. The nitro oxygen atom O(36), which acts as an acceptor in the intercomplex hydrogen bond, also forms a short contact (2.99 (1) Å) with itself across the center of symmetry at $(^1/_2, {}^1/_2, 0)$, Figure 4. Similar abuttings of two nitro groups are also found in the deoxyadenosine[5] and triacanthine[6] complexes. The intercomplex hydrogen bonding and the close proximity of the symmetry-related dinitro anions about Co(3) lead to the relatively tight packing scheme shown in Figure 4. The requirements leading to this packing scheme apparently cause the distortions observed in the dinitro anion about Co(3).

The interactions involving the dinitro anion containing Co(2) are less numerous. One of the oxygen atoms, O(26), of the nitro group interacts with C(8) of the purine ring of the complex cation [O(26)···C(8), O(26)···H(8) distances = 3.06 (1) and 2.71 Å, respectively]. A second notable interaction involves one of the coordinated acac oxygen atoms, O(22), and the methyl group at N(9) of the purine ligand [O(22)···C(9) = 3.41 (1) Å].

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Registry No. $[Co(acac)_2(NO_2)(1,9\text{-dimethyladeninium})][Co(acac)_2(NO_2)_2]$, 68630-57-9; $Na[Co(acac)_2(NO_2)_2]$, 14024-47-6.

Supplementary Material Available: Anisotropic thermal parameters, parameters for the hydrogen atoms, best plane calculations, and a list of observed and calculated structure factor amplitudes (37 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. B. Dunn and R. H. Hall in "Handbook of Biochemistry and Molecular Biology", Vol. 1, G. Fasman, Ed., 3rd ed., CRC Press, Cleveland, Ohio, 1975, p 65.
(2) J. A. McCloskey and S. Nishimura, *Acc. Chem. Res.* **10**, 403 (1977).
(3) A. Rich, *Acc. Chem. Res.*, **10**, 388 (1977).
(4) K. Hoogsteen, *Acta Crystallogr.*, **16**, 907 (1968).
(5) T. Sorrell, L. A. Epps, T. J. Kistenmacher, and L. G. Marzilli, *J. Am. Chem. Soc.*, **99**, 2173 (1977).
(6) T. Sorrell, L. A. Epps, T. J. Kistenmacher, and L. G. Marzilli, *J. Am. Chem. Soc.*, in press.
(7) N. J. Leonard and T. Fujii, *Proc. Natl. Acad. Sci. U.S.A.*, **51**, 73 (1964).
(8) L. J. Boucher and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).
(9) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(10) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).
(11) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(12) R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(14) Crystallographic programs employed include: Wehe, Busing, and Levy's ORABS; Busing, Martin, and Levy's ORFLS; Zalkin's FORDAP; Pippy and Ahmed's MEAN PLANE; Johnson's ORTEP. Calculations other than those specifically noted were performed with locally written programs.
(15) L. G. Marzilli and T. J. Kistenmacher, *Acc. Chem. Res.*, **10**, 146 (1977).
(16) T. J. Kistenmacher and L. G. Marzilli in "Metal-Ligand Interaction in Organic and Biochemistry", Part I, B. Pullman and N. Goldblum, Eds., D. Reidel, Dordrecht, 1977, pp 7–40.
(17) T. J. Kistenmacher, T. Sorrell, M. Rossi, C. C. Chiang, and L. G. Marzilli, *Inorg. Chem.*, **17**, 479 (1978).
(18) D. Voet and A. Rich, *Prog. Nucl. Acid. Res. Mol. Biol.*, **10**, 183 (1970).
(19) T. J. Kistenmacher, C. C. Chiang, L. A. Epps, and L. G. Marzilli, unpublished results.