

molecule with respect to the Ti–Cl and Ti–N directions are different in the three rings (Fig. 2). The 1- and 2-methylimidazole ligands [rings containing atoms N(1) and N(2), respectively] are bisectors with angles of approximately 45°, while the third molecule is parallel [6(2)°]. The dihedral angle between the *trans* methylimidazole ligands is 135.9(5)° which differs from that in $\text{TiCl}_3(\text{C}_5\text{H}_5\text{N})_3 \cdot \text{C}_5\text{H}_5\text{N}$, where the planes of the *trans* pyridines are at 90° (Jeffs, Small & Worrall, 1984b), although this comparison is not ideal since the methyl group bonded to the imidazole ring, in the packing of the unit cell, may have a different effect to the additional solvate molecule in the pyridine complex.

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Transition Metal Complexes with Hydrazides and Hydrazones. IV. Structure of *trans*-Diammine[2,3-butanedione bis(4-methoxybenzoylhydrazone)]cobalt(III) Nitrate Monohydrate

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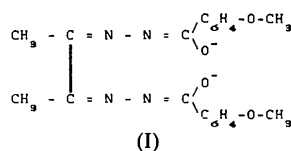
(Received 4 July 1990; accepted 18 December 1990)

Abstract. $[\text{Co}(\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_4)(\text{NH}_3)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$, $M_r = 553.42$, monoclinic, $P2_1/n$, $a = 15.820(2)$, $b = 10.156(1)$, $c = 17.127(1)$ Å, $\beta = 117.41(1)^\circ$, $V = 2442.8$ Å³, $Z = 4$, $D_x = 1.504$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.76$ mm⁻¹, $F(000) = 1152$, $T = 293$ K, final $R = 0.069$ for 2179 reflections with $I > 2\sigma(I)$. The coordination of the Co atom is distorted octahedral with *trans*-NH₃ groups. The quadri-dentate *N,N,O,O* ligand is equatorially disposed, forming three five-membered coplanar chelate rings. The O atoms of the NO₃ anion are disordered.

Introduction. Recent studies of hydrazones and their metal complexes are not only of theoretical but also

of practical importance. A great number of these compounds have found wide application in medicine, technology, analytical chemistry, etc. (Kitaev, 1977; Katyal & Dutt, 1975). The complexes with mono- and bishydrazones of diketones, such as diacetylhydrazones and acetylacetone hydrazones (Harrison & Nicholls, 1984; Khulbe, Kumar, Bhoon & Singh, 1984; James, McCleverty, McKenzie & Moore, 1985; Krimova, Ivanov & Ostankevich, 1986; Abu-El-Wafa, Gaber, Issa & Ismail, 1989) form a special class of compounds. In our previous work we described the structure of the square-planar Cu^{II} complex with acetylacetone 1-naphthoylhydrazone (Fazlić, Divjaković, Leovac & Chundak, 1991).

As a continuation of our studies of the complexes of these ligands, we report the structure of a newly synthesized Co^{III} complex with 2,3-butanedione bis(4-methoxybenzoylhydrazone), $[\text{Co}(L)(\text{NH}_3)_2]\cdot\text{NO}_3\cdot\text{H}_2\text{O}$, where L (I) is the dianion of the hydrazone ligand.



Experimental. The title compound was obtained by reacting stoichiometric amounts of warm methanol/ammonia solution containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 2,3-butanedione bis(4-methoxybenzoylhydrazone)- H_2L . The dark-red lath-shaped crystals are of poor quality, fragile and usually twinned. After inspection of a number of crystals by microscopy and film methods, a transparent crystal with approximate dimensions $0.08 \times 0.08 \times 0.40$ mm was isolated and used for data collection. Enraf-Nonius CAD-4 diffractometer, $\text{Mo } K\alpha$ radiation, graphite monochromator, cell parameters from least-squares fit of 23 reflections with $8 < \theta < 16^\circ$. Intensity data collection in $\omega/2\theta$ scan mode, scan width $(0.8 + 0.35\tan\theta)^\circ$ and for background determination 25% below and above this range, scan rate 1 to 7° min^{-1} in ω , $2\theta < 50^\circ$, h $0 \rightarrow 18$, k $0 \rightarrow 12$, l $-20 \rightarrow 17$, no significant variation of the two standard reflections measured every 60 min, data not corrected for absorption or extinction. 4731 reflections collected, after averaging 4223 unique ($R_{\text{int}} = 0.035$), of which 2179 with $I > 2\sigma(I)$. Structure solution by Patterson and difference Fourier syntheses, full-matrix least-squares refinement on F and $w = 1$, anisotropic thermal parameters for complex cation, isotropic for NO_3 anion and water O atoms. The occupancy factors for the O atoms of the disordered nitrate anion were first refined independently, then manually reset to give a total occupancy of 100% and finally fixed to 0.70 and 0.30, respectively, for the two orientations of the nitrate ion. H atoms were initially located in difference syntheses; their positions were adjusted to give C—H and N—H distances of 0.95 \AA and they were then allowed to ride on appropriate N or C atoms [$B(\text{H}) = 1.3 \times B_{\text{eq}}(\text{N,C})$]. However, the H atoms of the water molecule were fixed at positions obtained from the difference syntheses with isotropic thermal parameters fixed at $B = 6.0 \text{ \AA}^2$. 312 parameters, $R = 0.069$, $wR = 0.074$, max. $\Delta/\sigma < 0.02$, $\Delta\rho_{\text{max}} = 0.53$, $\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$, the goodness of fit, $S = 2.99$. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations performed on a PDP11/73 computer using

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}/B (\text{\AA}^2)$
Co	0.44757 (8)	0.2998 (1)	0.52451 (7)	2.95 (2)
O1	0.3483 (4)	0.4332 (6)	0.4836 (3)	3.4 (1)
O2	0.5094 (4)	0.2914 (6)	0.4501 (3)	3.5 (1)
O3	-0.0110 (5)	0.7550 (9)	0.4422 (4)	6.7 (2)
O4	0.7682 (4)	0.1096 (8)	0.2804 (4)	5.5 (2)
O5	0.3584 (9)	0.616 (1)	0.1013 (8)	7.3 (3)*
O6	0.423 (1)	0.491 (2)	0.209 (1)	10.7 (5)*
O7	0.3474 (8)	0.657 (1)	0.2222 (8)	6.9 (3)*
O5'	0.457 (2)	0.542 (3)	0.211 (1)	7.6 (6)*
O6'	0.321 (1)	0.566 (2)	0.208 (1)	6.2 (5)*
O7'	0.345 (1)	0.674 (2)	0.108 (1)	4.5 (4)*
OH	0.3130 (7)	0.288 (1)	0.2540 (7)	11.3 (3)*
N1	0.3345 (4)	0.3508 (7)	0.6029 (4)	3.5 (2)
N2	0.4081 (5)	0.2759 (7)	0.6082 (4)	3.5 (2)
N3	0.5310 (4)	0.1684 (7)	0.5823 (4)	3.0 (2)
N4	0.5915 (5)	0.1288 (7)	0.5494 (4)	3.4 (2)
N5	0.3531 (5)	0.1791 (8)	0.4421 (5)	4.1 (2)
N6	0.5409 (5)	0.4305 (8)	0.5979 (4)	3.5 (2)
N7	0.3758 (6)	0.590 (1)	0.1757 (6)	5.9 (2)*
C1	0.3074 (5)	0.4307 (9)	0.5341 (5)	3.1 (2)
C2	0.4556 (6)	0.1876 (9)	0.6679 (4)	3.3 (2)
C3	0.4367 (6)	0.158 (1)	0.7442 (5)	4.4 (2)
C4	0.5297 (6)	0.1234 (8)	0.6533 (5)	3.4 (2)
C5	0.5976 (7)	0.026 (1)	0.7132 (6)	4.5 (3)
C6	0.5730 (6)	0.200 (1)	0.4786 (5)	3.6 (2)
C7	0.2266 (5)	0.5189 (9)	0.5133 (5)	3.1 (2)
C8	0.1898 (6)	0.5955 (9)	0.4373 (5)	3.7 (2)
C9	0.1111 (6)	0.672 (1)	0.4156 (6)	4.6 (3)
C10	0.0669 (6)	0.677 (1)	0.4691 (5)	4.3 (2)
C11	0.1056 (6)	0.605 (1)	0.5461 (6)	4.9 (2)
C12	0.1832 (6)	0.526 (1)	0.5676 (5)	3.7 (2)
C13	-0.0548 (7)	0.769 (1)	0.4970 (6)	7.1 (3)
C14	0.6268 (5)	0.1734 (8)	0.4288 (5)	3.0 (2)
C15	0.7075 (6)	0.0996 (9)	0.4618 (5)	3.2 (2)
C16	0.7573 (6)	0.073 (1)	0.4158 (5)	4.4 (2)
C17	0.7248 (6)	0.125 (1)	0.3332 (5)	3.7 (2)
C18	0.6435 (6)	0.201 (1)	0.2974 (5)	4.6 (2)
C19	0.5931 (6)	0.2264 (9)	0.3439 (5)	3.7 (2)
C20	0.8444 (7)	0.020 (1)	0.3086 (7)	7.1 (3)

* Refined isotropically.

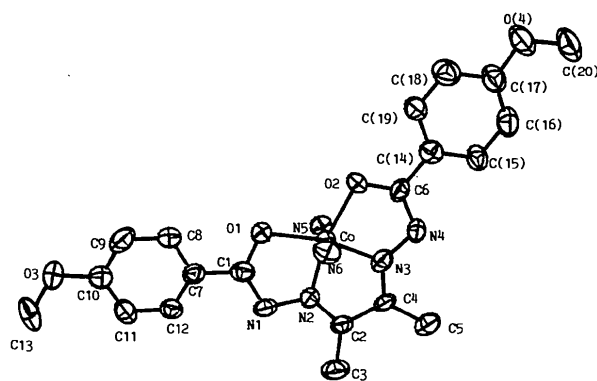
Enraf-Nonius SDP (Frenz, 1978). Final positional parameters of non-H atoms are given in Table 1,* selected bond distances and angles in Table 2. A perspective view of the complex cation, with atom-numbering scheme, is given in Fig. 1.

Discussion. The crystal structure of the title compound consists of discrete $[\text{Co}L(\text{NH}_3)_2]^+$ cations, nitrate anions and molecules of water. The L ligand is quadridentate, forming three fused five-membered chelate rings which lie in the equatorial plane. The two ammonia molecules occupy axial positions. The coordination of the Co atom is approximately octahedral, with distortions arising from the steric constraints in the L ligand. The complex cation has no crystallographically imposed geometry; however, most chemically equivalent bond distances and

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, least-squares planes, H-atom parameters and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53852 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°)

Co	O1	1.944 (4)	O5'	N7	1.239 (19)		
Co	O2	1.933 (3)	O6'	N7	1.251 (15)		
Co	N2	1.825 (4)	O7'	N7	1.331 (15)		
Co	N3	1.817 (5)	N1	N2	1.358 (6)		
Co	N5	1.946 (5)	N1	C1	1.329 (7)		
Co	N6	1.953 (5)	N2	C2	1.307 (7)		
O1	C1	1.298 (6)	N3	N4	1.376 (6)		
O2	C6	1.292 (7)	N3	C4	1.308 (6)		
O3	C10	1.356 (7)	N4	C6	1.321 (7)		
O3	C13	1.407 (7)	C1	C7	1.464 (7)		
O4	C17	1.372 (6)	C2	C3	1.498 (7)		
O4	C20	1.409 (8)	C2	C4	1.461 (8)		
O5	N7	1.201 (10)	C4	C5	1.471 (8)		
O6	N7	1.228 (14)	C6	C14	1.480 (7)		
O7	N7	1.274 (10)	C7	C8	1.393 (8)		
O1	Co	O2	111.3 (2)	N3	N4	C6	108.4 (4)
O1	Co	N2	82.2 (2)	O5	N7	O6	117 (1)
O1	Co	N3	166.4 (2)	O5	N7	O7	125.1 (9)
O1	Co	N5	87.4 (2)	O6	N7	O7	117.7 (9)
O1	Co	N6	90.2 (2)	O5'	O7	O6'	118 (1)
O2	Co	N2	166.5 (2)	O5'	N7	O7'	124 (1)
O2	Co	N3	82.3 (2)	O6'	N7	O7'	118 (1)
O2	Co	N5	86.9 (2)	O1	C1	N1	123.1 (5)
O2	Co	N6	89.5 (2)	O1	C1	C7	118.3 (5)
N2	Co	N3	84.3 (2)	N1	C1	C7	118.6 (5)
N2	Co	N5	93.5 (2)	N2	C2	C3	123.1 (5)
N2	Co	N6	90.9 (2)	N2	C2	C4	113.0 (4)
N3	Co	N5	93.2 (2)	C3	C2	C4	123.9 (5)
N3	Co	N6	90.2 (2)	N3	C4	C2	111.2 (5)
N5	Co	N6	174.7 (2)	N3	C4	C5	124.3 (5)
N2	N1	C1	108.6 (4)	C2	C4	C5	124.5 (5)
Co	O1	C1	108.3 (3)	O2	C6	N4	123.0 (5)
Co	O2	C6	109.0 (3)	O2	C6	C14	117.8 (5)
Co	N2	N1	117.8 (4)	N4	C6	C14	119.2 (5)
Co	N2	C2	115.1 (4)	O3	C10	C9	117.0 (6)
N1	N2	C2	127.1 (4)	O3	C10	C11	124.8 (6)
Co	N3	N4	117.3 (3)	O4	C17	C16	125.0 (6)
Co	N3	C4	116.4 (4)	O4	C17	C18	114.6 (5)
N4	N3	C4	126.2 (5)				

Fig. 1. View of [CoL(NH₃)₂]⁺ cation showing the atomic labelling scheme. H atoms are omitted for clarity.

the two methoxybenzoyl parts of the ligand closely resemble that of 4-methoxybenzoic acid (Colapietro & Domenicano, 1978). The two benzene rings C7–C12 and C14–C19 are inclined 6 (2) and 13 (1)°, respectively, to the mean plane of the fused chelate ring system.

The O atoms of the nitrate anions are statistically distributed over two positions with respective approximate occupancies 0.7 and 0.3. The least-squares mean planes through the atoms of the nitrate ions in the two orientations are inclined at 45° to each other.

There are many intermolecular O—H···O, N—H···O and N—H···N distances which satisfy the geometrical criteria for hydrogen bonding. Pairs of complex cations related by a centre of symmetry are linked by N—H···O hydrogen bonds. A weak N—H···N interaction connects these pairs into ribbons, running parallel to the *b* axis. In accordance with the observed statistical distribution of the nitrate ion, in both NH₃ ligands one H atom is found in a position which allows hydrogen bonding with an O atom in one or other orientation of the nitrate ion. Finally, the water molecule is connected by N—H···O and O—H···O hydrogen bonds to the cations and nitrate ions, respectively.

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angles differ by less than 3σ . The Co—O [av. = 1.939 (5) Å] and Co—N(NH₃) [av. = 1.950 (4) Å] distances are in the ranges usually reported. However, the Co—N(L) bonds of 1.817 (5) and 1.826 (4) Å are at the short end of Co^{III}—N distances. Reliably determined Co—N bond lengths shorter than 1.85 Å, (Cambridge Structural Database, 1989, version 3.4) are mainly found in organometallic nitrosyl complexes but also occur in Co^{III} oxime and imine complexes (Randaccio, Bresciani-Pahor, Toscano, & Marzilli, 1980; Peng, Wang, Wang & Shuang, 1981; Simonov, Zavodnik, Sharova, Dvorkin, D'yachenko & Stetsenko, 1984; Liaw, Peng, Chern & Sheu, 1986; Collins, Richmond, Santarsiero & Treco, 1986) and in a Co^{III} complex with a macrocyclic pentaaza ligand (Drew, Hollis & Yates, 1985). The three five-membered chelate rings are to a great extent planar and also almost coplanar (the maximum displacement of the atoms from the mean plane of the fused chelate ring system is 0.03 Å). The N—N and N—C bond distances in the outer chelate rings indicate charge delocalization. The bond lengths and angles in the rest of the ligand are in agreement with the atom type and hybridization. The geometries of

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Structure of 4,5-Epoxy-3-methoxy-N, α,α -trimethylmorphinan-5,8-diene-7 α -methanol

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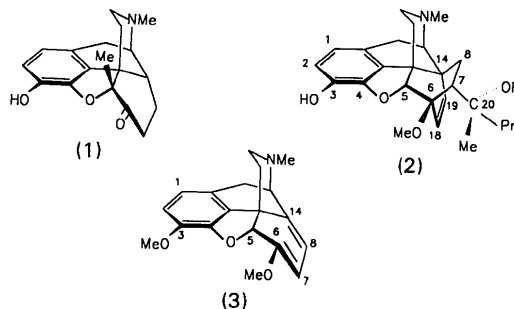
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Abstract. C₂₁H₂₅NO₃, $M_r = 339.43$, orthorhombic, $P2_12_12_1$, $a = 9.830$ (1), $b = 10.878$ (1), $c = 16.781$ (1) Å, $V = 1794.4$ (3) Å³, $Z = 4$, $D_x = 1.256$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, $\mu = 6.3$ cm⁻¹, $F(000) = 728$, $T = 295$ K, $R = 0.046$ for 2364 reflections [$I > 2.5\sigma(I)$]. The title compound is one of three isomeric morphinans, which were obtained from deprotonation of the 5-position of 6-dimethoxythebaine with butyllithium, followed by reaction of the resultant anion with acetone. The dimethylmethanol substituent is in the 7 α -position of the morphinan skeleton and its hydroxyl group forms an intermolecular hydrogen bond with the lone pair of the tertiary nitrogen, resulting in an infinite hydrogen-bonded chain running in the b direction. An interesting feature of the title compound is the C(5)—C(6) double bond that does not seem to limit the substitution possibilities on the ring.

Introduction. Metopon (1), a semisynthetic analgesic, exhibits remarkable pharmacological properties, namely an increase of antinociceptive action with a parallel decrease of unwanted side effects (Casy & Parfitt, 1986). Etorphine (2) is, like metopon (1), a

semisynthetic analgesic, but it shows an extraordinarily high analgesic activity (1000 \times morphine) (Lewis, Bentley & Cowan, 1971). Therefore an interesting biological activity is expected with the introduction of an etheno bridge in metopon (Woudenberg, Lie & Maat, 1990) and analogues.



We have investigated the influence of substituents at the 5 β -position of thebaine (3) on its pharmacological characteristics and on the course of the Diels-Alder reaction, for which we introduced a dimethylmethanol group at the 5 β -position of thebaine (3) (Woudenberg, Lie & Maat, 1991) according to known procedures (Gates, Boden & Sundararaman, 1989).

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