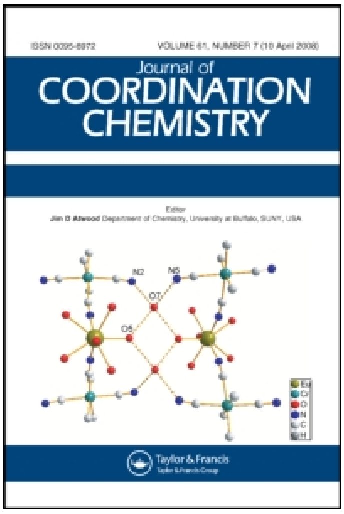

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SYNTHESIS, SPECTROSCOPIC AND STRUCTURAL STUDY OF *TRIS*[ETHYL-2-(HYDROXYIMINO) ACETOACETATO]COBALT(III)

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SYNTHESIS, SPECTROSCOPIC AND STRUCTURAL STUDY OF *TRIS*[ETHYL-2-(HYDROXYIMINO) ACETOACETATO]COBALT(III)

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The preparation and characterization of the title complex, [CoL_3], is reported. The crystal structure determination shows that the three ligands each coordinate *via* the ketonic oxygen and oximic nitrogen atoms such that the overall configuration about the cobalt atom is *fac*. Crystals of [CoL_3] are monoclinic, space group $P2_1/n$ with unit cell dimensions $a = 14.234(6)$, $b = 8.229(3)$, $c = 19.654(8)$ Å, $\beta = 96.99(4)°$, $V = 2285(1)$ Å^3, $Z = 4$. The structure was refined by a full-matrix least-squares procedure to $R_w = 0.045$ for 1936 observed reflections.

KEYWORDS: cobalt(III), stereochemistry, crystal structure

INTRODUCTION

A number of isonitrosoketones and related nitrosophenol ligands are used as analytical reagents.[1] Transition metal complexes of such ligands[2,3] are potential models for metal binding sites in ferroverdin.[4,5] They also find industrial applications as dyes and as light-absorbing agents for the acceleration of the solar evaporation of water.[6] In view of the importance of metal complexes of isonitrosoketones and nitrosophenols and as a continuation of previous interest in this field,[7–9] the synthesis of the title compound, tris[ethyl-2-(hydroxyimino)-acetoacetato]cobalt(III), hereafter [CoL_3], its spectroscopic characterization and X-ray crystal structure determination have been undertaken; this is the first crystal structure of a complex containing L, *i.e.*, the anion of MeC(O)C(NOH)C(O)OEt. Tanaka and co-workers[10] have reported that the preparation of related [$Co(RC(O)C(NO)R')_3$] complexes are relatively facile when R and R′ are aromatic groups but decidedly less so when these groups are aliphatic. The present complex has been shown to be stable in both in solution and in solid state.

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EXPERIMENTAL

Materials

MeC(O)C(NOH)C(O)OEt (LH) was prepared by the method of Adkins and Reeves.[11] Analytical grade hydrated cobaltous acetate was used.

Instrumentation

Infrared spectra were obtained on a Perkin Elmer 1430 spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ solution using TMS as an internal reference on a Varian EM 390L spectrophotometer. Mass spectra were recorded in the EI ionization mode at 70 eV on a VG micromass 7070F. C, H, and N were determined microanalytically on a Perkin Elmer 2400 CHN analyzer.

Preparation

When an ethanolic solution of LH was mixed with an aqueous solution of cobaltous acetate (2:1) and stirred for 3 h an orange-red solid separated out. This was filtered, washed with water and dried. Ruby-red crystals of $[CoL_3]$ were obtained in almost quantitative yield on recrystallization from a mixture of acetone and isopropanol; m. p. 159–160°C. The complex is insoluble in water but readily soluble in organic solvents such as acetone, chloroform, benzene, methanol and ethanol. Analysis, found: C, 40.50; H, 4.38; N, 7.85%. Calcd. for $C_{18}H_{24}CoN_3O_{12}$: C, 40.53; H, 4.54; N, 7.89 %. IR: ν(C=O) 1715, ν(C=N) + ν(C=C) 1535, ν(N-O) 1290 and ν(M-N) 630 cm^{-1}. ^{1}H NMR: δ 4.55 (q, OCH_2), 2.95 (s, CH_3), 1.40 ppm (t,OCH_2CH_3). Mass spectra: (M/Z rel. intensity, fragment) 533, 0.9%, $[CoL_3]^+$; 375, 3.7 $[CoL_2]^+$; 131, 48.0, [LH-CO]; 113, 32.9, $[L\text{-}OC_2H_5]^+$; 54, 100, $[CH_2{=}C{=}C{=}O]^+$. The absorption band at 340 nm, observed in both benzene and methanol solution, is assigned to the charge transfer from the cobalt atom to the ligand by analogy with literature results:[12] *d-d* transitions were masked by charge transfer bands.

Crystallography

Intensity data for a crystal (0.05 × 0.24 × 0.37 mm) were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromatized MoKα radiation, $\lambda = 0.71073$ Å, employing the ω:2θ scan technique such that θ_{max} was 27.5°. The 6052 data were corrected for Lorentz and polarization effects[13] and for absorption effects (range of transmission factors: 0.940–1.115).[14] Of the reflections measured, 5829 were unique and of these 1936 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for $[CoL_3]$, $C_{18}H_{24}CoN_3O_{12}$, $M = 533.3$, monoclinic, space group $P2_1/n$, $a = 14.234(6)$, $b = 8.229(3)$, $c = 19.654(8)$ Å, $\beta = 96.99(4)°$, $V = 2285(1)$ Å^3, $Z = 4$, $D_{calc} = 1.550$ g cm^{-3}, $\mu = 8.19$ cm^{-1}.

The structure was solved by direct methods[15] and refined by a full-matrix least-squares procedure based on F.[13] Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions. Some disorder in the structure is evident in the short C(15)-C(16) bond distance [1.24(1) Å]; however, no evidence for an alternate position for this residue was found. At convergence, $R = 0.052$ and $R_w = 0.045$ (sigma weights). The analysis of variance showed no special features and the maximum electron density peak in the final difference map was 0.36 e Å^{-3}. Fractional atomic coordinates are listed in Table 1, selected interatomic parameters are given in Table 2 and the numbering scheme employed is shown in Figure 1 which was drawn using the ORTEP program with 40% probability ellipsoids.[16] Listings of thermal parameters, H atom parameters, all bond distances and angles, and structure factor amplitudes are available on request from ERTT.

RESULTS AND DISCUSSION

The reaction of MeC(O)C(NOH)C(O)Me (L′H) with cobaltous salts was reported by Taylor and Ewbank[17] to form an orange-red solid of formula [CoL′$_3$]. On the basis of analytical and molecular weight measurements a structure was assigned in which the L′ anion chelated the cobalt atom *via* the nitroso oxygen and one of the carbonyl

Table 1 Fractional atomic coordinates for [CoL$_3$].

Atom	*x/a*	*y/b*	*z/c*
Co	0.2613(1)	0.4064(1)	0.0991(1)
O(11)	0.1691(3)	0.5726(6)	0.0919(2)
O(13)	0.2761(3)	0.3125(6)	-0.0328(2)
O(14)	0.0505(4)	0.5521(9)	0.1099(3)
O(15)	0.1935(4)	0.5089(7)	0.1336(3)
O(21)	0.3589(3)	0.5630(6)	0.0950(2)
O(23)	0.3533(3)	0.1118(7)	0.1080(3)
O(24)	0.5904(5)	0.2401(10)	0.1592(3)
O(25)	0.5414(4)	0.1484(8)	0.0583(3)
O(31)	0.2723(3)	0.4202(6)	0.1960(2)
O(33)	0.1292(3)	0.1701(6)	0.0628(2)
O(34)	0.0352(3)	0.1660(6)	0.2447(2)
O(35)	0.0648(4)	-0.0028(7)	0.1630(2)
N(13)	0.2359(4)	0.4042(8)	0.0041(3)
N(23)	0.3612(4)	0.2602(8)	0.1040(3)
N(33)	0.1703(4)	0.2496(7)	0.1107(3)
C(12)	0.1371(4)	0.6028(9)	0.0321(4)
C(12′)	0.0697(5)	0.7380(10)	0.0191(4)
C(13)	0.1697(5)	0.5093(9)	-0.0202(3)
C(14)	0.1314(6)	0.5257(10)	-0.0925(4)
C(15)	0.1573(8)	0.5220(15)	-0.2073(4)
C(16)	0.2140(11)	0.5932(27)	-0.2400(6)
C(22)	0.4388(6)	0.4995(12)	0.1009(3)
C(22′)	0.5223(5)	0.6044(11)	0.1018(4)
C(23)	0.4455(5)	0.3299(11)	0.1057(3)
C(24)	0.5323(6)	0.2339(12)	0.1118(5)
C(25)	0.6233(6)	0.0402(11)	0.0576(5)
C(26)	0.6957(6)	0.1220(12)	0.0287(6)
C(32′)	0.2055(5)	0.3428(9)	0.2947(4)
C(32)	0.2103(5)	0.3356(9)	0.2202(3)
C(33)	0.1511(4)	0.2356(8)	0.1751(3)
C(34)	0.0771(5)	0.1323(9)	0.1984(4)
C(35)	-0.0056(6)	-0.1171(11)	0.1828(4)
C(36)	-0.0945(6)	0.0808(13)	0.1401(5)

Table 2 Selected bond distances (Å) and angles (°) for $[CoL_3]$.

Co-O(11)	1.889(5)	Co-O(21)	1.904(5)
Co-O(31)	1.894(4)	Co-N(13)	1.859(5)
Co-N(23)	1.857(6)	Co-N(33)	1.861(6)
O(11)-C(12)	1.232(7)	O(13)-N(13)	1.234(6)
O(14)-C(14)	1.180(8)	O(15)-C(14)	1.276(8)
O(15)-C(15)	1.481(9)	O(21)-C(22)	1.244(8)
O(23)-N(23)	1.230(7)	O(24)-C(24)	1.168(9)
O(25)-C(24)	1.285(9)	O(25)-C(25)	1.468(8)
O(31)-C(32)	1.261(7)	O(33)-N(33)	1.234(6)
O(34)-C(34)	1.180(8)	O(35)-C(34)	1.312(8)
O(35)-C(35)	1.460(8)	N(13)-C(13)	1.326(8)
N(23)-C(23)	1.326(8)	N(33)-C(33)	1.333(7)
O(11)-Co-O(21)	90.6(2)	O(11)-Co-O(31)	90.2(2)
O(11)-Co-N(13)	83.3(2)	O(11)-Co-N(23)	173.8(3)
O(11)-Co-N(33)	91.4(2)	O(21)-Co-O(31)	91.8(2)
O(21)-Co-N(13)	91.0(2)	O(21)-Co-N(23)	83.2(2)
O(21)-Co-N(33)	175.2(2)	O(31)-Co-N(13)	173.0(2)
O(31)-Co-N(23)	91.0(2)	O(31)-Co-N(33)	83.8(2)
N(13)-Co-N(23)	95.7(3)	N(13)-Co-N(33)	93.6(2)
N(23)-Co-N(33)	94.9(3)	Co-O(11)-C(12)	113.0(5)
Co-O(21)-C(22)	112.0(5)	Co-O(31)-C(32)	111.8(4)
Co-N(13)-C(13)	123.3(5)	Co-N(13)-C(13)	113.5(5)
Co-N(23)-O(23)	124.8(5)	Co-N(23)-C(23)	114.0(6)
Co-N(33)-O(33)	123.1(4)	Co-N(33)-C(33)	113.8(5)
C(14)-O(15)-C(15)	115.2(7)	C(24)-O(25)-C(25)	120.0(7)
C(34)-O(35)-C(35)	117.2(6)	O(13)-N(13)-C(13)	123.2(6)
O(23)-N(23)-C(23)	121.2(7)	O(33)-N(33)-C(33)	123.1(6)

oxygen atoms; the *bis* complex had been reported earlier by Ponzio.[18] For the related complex with α-benzil monoxime, PhC(=O)C(=NO)Ph, Pfeiffer and Richarz proposed a structure which involved coordination *via* the oximic nitrogen atom (instead of the oximic oxygen atom) as well as by the carbonyl group.[19] In the case of the title complex, $[CoL_3]$, four possible modes of coordination of the L anion can be postulated which are consistent with the spectroscopic results. The cobalt atom may be chelated by the ketonic oxygen atom and the oxime oxygen or nitrogen atom or may be chelated by the ester carbonyl oxygen atom and either of the oxime atoms. It is noteworthy that despite the variety of isomers that may be adopted by this complex only one has been isolated from the reaction mixture in almost quantitative yield (see Experimental).

The presence of three equivalent coordinated ligands in solution is revealed by the ^{1}H NMR measurements. The possibility of geometrical changes within the time scale of the NMR measurement may be ruled out.[20] The inertness of the low spin Co(III) complex is not in favour of a rapid equilibrium *fac*↔*mer* with bond-rupture at room temperature.[21] The crystal structure determination of $[CoL_3]$ was therefore performed to determine unambiguously the structure of the complex.

The molecular structure of $[CoL_3]$ is shown in Figure 1 and selected interatomic parameters are listed in Table 2. The lattice is comprised of discrete molecules of the complex with the closest intermolecular contact between non-hydrogen atoms being 3.105(9) Å for O(23)...C(32′)′ (symmetry operation: $0.5 - x$, $-0.5 + y$, $0.5 - z$). The cobalt atom is chelated by three L anions which each coordinate *via* the ketonic oxygen and the oximic nitrogen atoms. The three oxygen atoms define

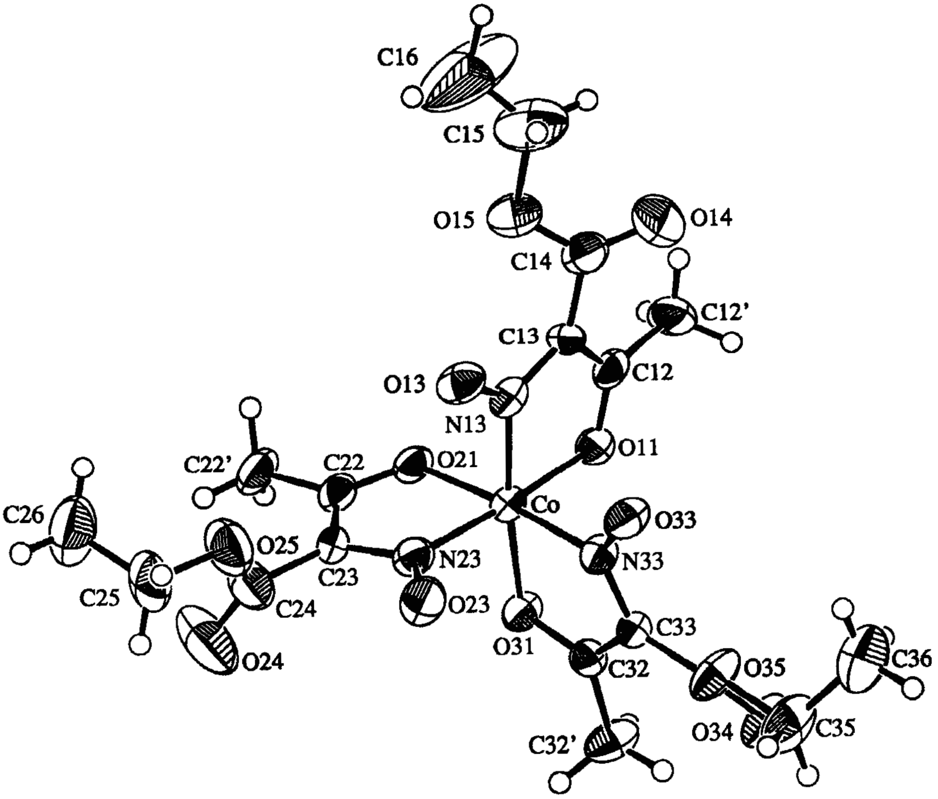

Figure 1 Molecular structure and crystallographic numbering scheme for [CoL_3].

one of the triangular faces in a distorted octahedral geometry about the cobalt atom and hence the configuration about the metal is *fac*.

The molecule has approximate three-fold symmetry and the ligands coordinate in a regular manner. The maximum distortion from the ideal octahedral geometry is found in the O(31)-Co-N(13) angle of 173.0(2)°. The O-Co-N chelate angles lie in the range 83.2(2) to 83.8(2)° and, as a result of their restricted bites, are responsible, in part, for the distortions from the ideal geometry; the other factor concerns the disparate Co-O or -N separations. The Co-O bond distances are equivalent within experimental error [range: 1.894(4) to 1.904(5) Å] and are longer than the Co-N bond distances [1.857(6) to 1.861(6) Å] which are also equal to each other. The result of the mode of coordination of the L anions is the formation of five-membered CoOCCN rings. The mean deviation of the five atoms from each of the planes is 0.008(5), 0.019(5) and 0.037(5) Å, respectively, and the dihedral angles between each of the planes are 91.8, 90.2 and 88.7°, respectively, emphasizing the regular disposition of the ligands. Other parameters associated with the ligands are as expected (see Experimental).

A crystal structure is available for the closely related complex, *fac-tris*(pentane-2,3,4-trione-3 -oximato)cobalt(III) which also has a *fac-tris* (N, O-chelate) configuration.[9] In this complex, for which there are two molecules in the crystallographic asymmetric unit, the Co-O bond distances range from 1.915(7) to 1.937(6) Å and the Co-N bond lengths lie in the range 1.864(9) to 1.90(1) Å, *i.e.*, slightly longer than the comparable bond in [CoL_3], although the relatively high errors associated with these parameters are noted.

Acknowledgements

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