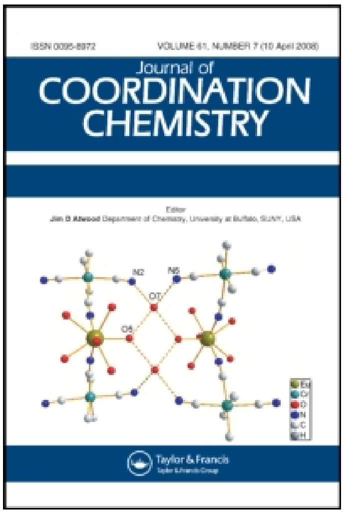

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SYNTHESIS AND X-RAY STRUCTURE OF TRIS[1-PHENYL-2-(HYDROXIMINO)-1,3-BUTANEDIONATO]COBALT(III) - A STRUCTURAL ANALOGUE OF NATURALLY OCCURRING FERROVERDIN

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SYNTHESIS AND X-RAY STRUCTURE OF TRIS[1-PHENYL-2-(HYDROXIMINO)-1,3-BUTANEDIONATO]COBALT(III) – A STRUCTURAL ANALOGUE OF NATURALLY OCCURRING FERROVERDIN

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The preparation and characterisation of the title complex, CoL_3, is reported. The crystal structure determination shows that the complex has three-fold symmetry and that the three ligands each coordinate *via* the ketonic oxygen (Co-O 1.931(4) Å) and oximic nitrogen atoms (Co-N 1.892(4) Å) such that the overall configuration about the cobalt atom is *fac*. Crystals of CoL_3 are trigonal, space group $R3c$, $a = 18.645(5)$, $c = 14.08(1)$ Å, $V = 4237(2)$ Å^3 and $Z = 6$. The structure was refined by a full-matrix least-squares procedure to $R_w = 0.031$ for 741 observed reflections.

KEYWORDS: cobalt(III), stereochemistry, crystal structure, ferroverdin

INTRODUCTION

Cobalt(III) complexes continue to receive attention[1–4] owing to cobalt(III) complexes having played a pivotal role in the development of inorganic chemistry, the presence of a cobalt(III) centre in vitamin B_{12}, and the use of cobalt(III) complexes are catalysts in the synthesis and hydrolysis of peptides.[5,6] Further, a number of isonitrosoketones and related nitrosophenol ligands are used as analytical reagents.[7] Transition metal complexes of the latter ligands[8,9] are potential models for metal binding sites in the naturally occurring, iron-containing pigment ferroverdin.[10,11] They also find industrial applications as dyes and as light-absorbing agents for the acceleration of the solar evaporation of water.[12] In view of the general importance of cobalt(III) complexes and of the metal complexes of isonitrosoketones and nitrosophenols, an investigation of their chemistry and structural characteristics has been undertaken. The synthesis, spectroscopic characterisation and X-ray structure determination of tris[methyl-2-(hydroxyimino) acetoacetato]cobalt(III) has been

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reported recently[13] as has the characterisation of tris[ethyl-2-(hydroxyimino) acetoacetato]cobalt(III).[14] As an extension of these previous studies, the preparation, spectroscopic characterisation and crystal structure determination of the tris[1-phenyl-2(hydroxyimino)-1,3-butanedionato]cobalt(III) complex, hereafter CoL_3, is reported herein.

EXPERIMENTAL

Synthesis

The ligand 1-phenyl-1,2,3-butanetrione 2-oxime was prepared according to the literature procedure.[15] When an ethanolic solution of the ligand (2 molar equivalents) was mixed with an aqueous solution of 1.05 molar equivalents of cobaltous acetate (analytical grade) and stirred for two hours, an orange-yellow solid precipitated out. The solid, CoL_3, was filtered, washed with water and air-dried; the yield was quantitative. Single crystals suitable for the X-ray study were grown by the slow evaporation of an acetone/chloroform (1/1) solution of the compound.

Instrumentation

Infrared spectra were obtained on a Perkin Elmer 1430 spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ solution using TMS as internal reference on a Varian EM 390L spectophotometer. C, H, and N were determined microanalytically on a Perkin Elmer 2400 CHN analyser. Details of the characterisation may be found in Table 1.

Crystallography

Intensity data for an orange crystal (0.16x0.24x0.24 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 2378 measured data were corrected for Lorentz and polarisation effects[16] and for absorption effects (range of transmission factors: 0.945–1.080).[17] Of the reflections measured, 1201 were unique and of these 741 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Table 1 Physico-chemical data for CoL_3.

Colour/m.p.	Orange-red needles, 215°C (dec.)
Solubility	Insoluble in water but soluble in conventional organic solvents
Elemental analyses	Found: C, 57.15; H, 3.88; N, 6.75%. Calcd. for $C_{30}H_{24}CoN_3O_9$: C, 57.23; H, 3.82; N, 6.68%.
IR (cm^{-1})	$\nu(C=O)$ 1655, $\nu(C=N)$ + $\nu(C=O)$ 1575, $\nu(N-O)$ 1300
^1H NMR (δ, ppm)	2.50 (s, CH_3); 770 (m, C_6H_5)
^{13}C NMR (δ, ppm)	209.2(Me*C*=O); 187.3 (Ph*C*=O); 153.7 (*C*=N); 135.3, 134.2, 129.4, 129.0 (Ph); 25.9 (Me)

Crystal data for CoL_3, $C_{30}H_{24}CoN_3O_9$, M = 629.5, trigonal, space group $R3c$, a = 18.645(5), c = 14.08(1) Å, V = 4237(2) Å^3, Z = 6, D_{calc} = 1.480 g cm^{-3}, μ = 6.69 cm^{-1}.

The structure was solved by direct methods[18] and refined by a full-matrix least-squares procedure based on F.[16] Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions. At convergence, $R = 0.031$ and $R_w = 0.031$ (sigma weights). The absolute structure was determined by refining the inverted structure and comparing the residuals. The analysis of variance showed no special features and the maximum electron density peak in the final difference map was 0.18 e Å^{-3}. Fractional atomic coordinates are listed in Table 2, selected interatomic parameters are given in Table 3 and the numbering scheme employed is shown in Figure 1 which was drawn with the ORTEP program with 30% probability ellipsoids.[19] 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

Whereas Ponzio[20] reported the formation of a cobaltous complex with 1-phenyl-1,2,3-butanetrione 2-oxime (as with other derivatives), Taylor and Ewbank[2] reported the cobaltic complex with the same sligand. The molecular weight determination of the complex in benzene solution, *i.e.*, 540, is lower than the theoretical value of 629 and therefore some doubt as to its preparation exists. The elemental analysis of the complex reported here (see Table 1) corresponds to the proposed formula $Co(C_{10}H_8NO_3)_3$, indicating that the cobalt(II) precursor has been oxidised to cobalt(III). On the basis of infrared results, which show a lowering of the $C=O$ stretching frequency and an increase in the N-O stretching frequency, as compared to the corresponding values of the free ligand, coordination to the cobalt atom *via* the nitrogen atom and one of the carbonyl oxyten atoms is indicated. The possibility of *fac* or *mer* isomers also exists. Support for the *fac* isomer is gained

Table 2 Fractional atomic coordinates for CoL_3.

Atom	*x/a*	*y/b*	*z/c*
Co	0	0	0.1554(-)
O(1)	-0.0184(2)	0.0739(2)	0.0762(2)
O(3)	0.1040(2)	0.1005(2)	0.3010(3)
O(4)	0.1690(2)	0.3036(2)	0.1926(3)
N(3)	0.0651(2)	0.0970(3)	0.2276(3)
C(2)	0.0219(3)	0.1477(3)	0.1039(3)
C(2')	0.0207(3)	0.2136(3)	0.0456(4)
C(3)	0.0665(3)	0.1643(3)	0.1910(4)
C(4)	0.1135(3)	0.2477(3)	0.2375(3)
C(5)	0.0877(3)	0.2615(3)	0.3312(4)
C(6)	0.0204(3)	0.1999(3)	0.3794(4)
C(7)	-0.0043(4)	0.2156(4)	0.4658(5)
C(8)	0.0378(4)	0.2940(4)	0.5038(4)
C(9)	0.1065(4)	0.3555(3)	0.4585(4)
C(10)	0.1310(3)	0.3397(3)	0.3720(4)

Table 3 Selected bond distances (Å) and angles (°) for $\mathrm{CoL_3}$.[*]

Co-O(11)	1.931(4)	Co-N(3)	1.892(4)
O(1)-C(2)	1.255(6)	O(3)-N(3)	1.244(5)
O(4)-C(4)	1.216(5)	N(3)-C(3)	1.346(6)
C(2)-C(2')	1.487(6)	C(2)-C(3)	1.425(7)
C(3)-C(4)	1.500(6)	C(4)-C(5)	1.470(6)
O(1)-Co-O(1)'	90.1(2)	O(1)-Co-N(3)	83.5(2)
O(1)-Co-N(3)'	92.9(2)	O(1)-Co-N(3)″	172.9(2)
N(3)-Co-N(3)'	93.9(2)	Co-O(1)-C(2)	112.4(3)
Co-N(3)-O(3)	125.1(3)	Co-N(3)-C(3)	112.9(3)
O(3)-N(3)-C(3)	121.9(4)	O(1)-C(2)-C(3)	118.1(4)
N(3)-C(3)-C(2)	112.9(4)	N(3)-C(3)-C(4)	121.9(4)
C(3)-C(4)-O(4)	117.9(4)	C(3)-C(4)-C(5)	120.1(4)

[*] Symmetry operations: one prime: $-y, x-y, z$; two primes: $-x+y, -x, z$.

from the ^{1}H NMR spectrum which reveals one resonance only in the methyl region. Geometrical exchange on the ^{1}H NMR time scale may be excluded[22] as the inertness of the low spin cobalt(III) complex is not in favour of a *fac* $\rightleftharpoons$ *mer* equilibrium involving bond rupture at room temperature.[23] The electronic spectrum, recorded in both methanol and chloroform solutions, reveal charge-transfer

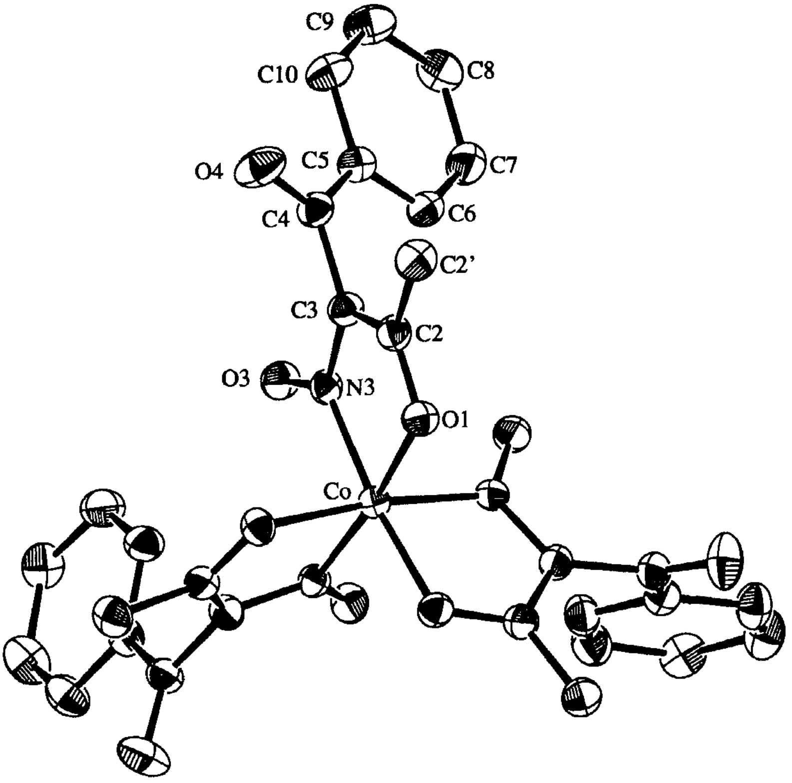

Figure 1 Molecular structure and crystallograpic numbering scheme for $\mathrm{CoL_3}$.

transitions within the range found for other closely related complexes;[24] the charge-transfer bands obscure the *d-d* bands. A crystal structure analysis of CoL_3 was undertaken in order to provide precise geometric parameters for this complex.

The molecular structure of CoL_3 is illustrated in Figure 1 and selected interatomic parameters are listed in Table 3. The cobalt atom is located on a crystallographic three-fold axis and thus there is only one independent ligand anion as labelled in Figure 1. There are no significant contacts in the crystal lattice with the closest non-hydrogen contact occurring between the O(4) and C(8)‴ atoms of 3.167(7) Å (symmetry operation: $-x+y,\ +y,\ -0.5+z$). From the crystallographic symmetry, a *fac* isomer is implied. The Co-O(1) and Co-N(3) bond distances are 1.931(4) and 1.892(4) Å, respectively and the O(1)-Co-N(3) chelate angle is 90.1(1)°. The geometry about the cobalt atom is slightly distorted from the ideal octahedral with the maximum distortion being manifested in the O(1)-Co-N(3)″ angle of 172.9(2)° (symmetry operation: $-x+y, -x, z$). The resultant $\overline{\text{CoOCCN}}$ ring that is formed upon chelation of the anion is effectively planar with the mean deviation of the atoms from the least-squares plane through them being 0.018 Å. The ligand itself is not planar, however, as seen in the magnitude of the N(3)/C(3)/C(4)/O(4) and N(3)/C(3)/C(4)/C(5) torsion angles of 119.0(5) and -65.8(6)°, respectively. The length of the C(3)-C(4) bond (1.500(6) Å) also indicates the possibility of free rotation about this bond and the lack of conjugation between the benzyl group and the remaining portion of ligand. By contrast, there is strong evidence for the delocalisation of π-electron density over the O(3)-N(3)-C(3)-C(2)-O(1) atoms. This is indicated, in particular, by the magnitude of the N(3)-C(3) and C(2)-C(3) bond distances of 1.346(6) and 1.425(7) Å, respectively. The present report detailing the crystal structure for CoL_3 enables a comparison of the derived interatomic parameters for three complexes with the general formula $Co[RC(=O)C(=NO)C(=O)Me]_3$, R = Ph (this work), Me,[25] and OEt.[14]

The three structures each feature a *fac-tris* (*N, O*-chelate) configuration. In the absence of steric constraints in these complexes, the *fac* isomer would be preferred to accommodate the complementary bonding requirements of the nitrogen and oxygen atoms which occupy *trans* positions. The range of Co-O bond distances in the R = OEt structure is 1.894(4) to 1.904(5) Å and the range of Co-N bond distances is 1.857(6) to 1.861(6) Å.[14] The comparable ranges for the R = Me complex, for which two independent molecules comprise the asymmetric unit, are 1.915(7) to 1.937(6) Å and 1.864(9) to 1.90(1) Å, respectively.[25] Although the respective ranges overlap for the R = Me and Ph compounds, the increase in the Co-O and Co-N bond lengths in the three complexes may be correlated with decreasing inductive effect of the R groups in the order Ph>Me>OEt. The slight differences in the coordinating abilities of the anions are also reflected in small changes associated with the N(3)/C(3)/C(2)/O(2) torsion angles that decrease from 6.1° for R = Ph, to 3.4° for R = Me and 1.8° for R = OEt (average values).

Acknowledgements

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References

1. L.J. Charbonniere, G. Bernardinelli, C. Piguet, A.M. Sargeson and A.F. Williams, *J. Chem. Soc., Chem. Commun.*, 1419 (1994).
2. R.J. Geue, A. Höhn, S.F. Ralph, A.M. Sargeson and A.C. Willis, *J. Chem. Soc., Chem. Commun.*, 1513 (1994).
3. R.J. Doyle, G. Salem and A.C. Willis, *J. Chem. Soc., Chem. Commun.*, 1587 (1994).
4. Y. Gök, H.B. Senturk, U. Ocak and H. Kantekin, *J. Chem. Res. (S)*, 258 (1994); *J. Chem. Res. (M)*, 1567 (1994).
5. D.A. Buckingham, L.G. Marzilli and A.M Sargeson, *J. Am. Chem. Soc.*, **89**, 2772 (1967).
6. D.A. Buckingham, J.P. Collman, D.A.R. Happer and L.G. Marzilli, *J. Am. Chem. Soc.*, **89**, 1082 (1967).
7. (a) F.J. Welcher, "Organic Analytical Reagents", (Van Nostrand, New York, 1948), Vol. 3, p. 252; (b) F. Feigl, "Chemistry of Specific, Selective, Sensitive Reactions", (Academic Press, New York, 1948), p. 208.
8. "Comprehensive Coordination Chemistry - The Synthesis, Reactions, Properties and Applications of Coordination Compounds", G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds), (Pergamon Press, Oxford, 1987), p. 797.
9. P. Basu and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 809 (1992).
10. A. Ballio, S. Barcellona, E.B. Chain, A. Tonolo, L. Vero-Barcellona, *Proc. Royal Soc. London, Ser. B*, **161**, 384 (1964).
11. S. Candeloro, D. Grdenic, N. Taylor, B. Thompson, M. Viswamitra and D.C. Hodgkin, *Nature*, **224**, 589 (1969).
12. "The Chemistry of Synthethic Dyes", K. Venkataraman (Ed.), Academic Press, New York, 1952), p. 401.
13. R.P. Sharma, V. Gupta, K.K. Bhasin, M. Quiros and J.M. Salas, *Acta Cryst.*, **C50**, 1875 (1995).
14. R.P. Sharma, V. Gupta, K.K. Bhasin and E.R.T. Tiekink, *J. Coord. Chem.*, **33**, 117 (1994).
15. J.F. Hansen and J.L. Flippen-Andersons, *J. Org. Chem.*, **50**, 3955 (1985).
16. TeXsan, Structure Analysis Package, (Molecular Structure Corporation, Texas, 1992).
17. N. Walker and D. Stuart, *Acta Cryst.*, **A39**, 158 (1983).
18. G.M. Sheldrick, "SHELXS86. Program for the automatic solution for crystal structure", (Göttingen University, Germany, 1986).
19. C.K. Johnson, ORTEPII, *Report 5138, Oak Ridge National Laboratory*, Tennessee (1976).
20. G. Ponzio, *Gazetta*, **52**, 285 (1928).
21. T.W.J. Taylor and E.K. Ewbank, *J. Chem. Soc.*, 288 (1926).
22. P. Basolo and R.G. Pearson, "Mechanisms of Inorganic Reactions", 2 Edn (Wiley, New York, 1967), p. 134.
23. S.S. Eaton and G.R. Eaton, *J. Am. Chem. Soc.*, **95**, 1825 (1973).
24. C. Matsumoto and K. Shinara, *Nippon Kagaku Zasshi*, **88**, 340 (1967) [CA: **67**, 58963z, 1964].
25. B.N. Figgis, C.L. Raston, R.P. Sharma and A.H. White, *Aust. J. Chem.*, **31**, 2437 (1978).