Howatson, J. & Grev, D. M. (1975). *J. Inorg. Nucl. Chem.* **37**, 1933–1935.
Jayadevan, N. C., Singh Mudher, K. D. & Chackraburtty, D. M. (1975). *Acta Cryst.* B**31**, 2277–2280.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Lenner, M. (1978). *Acta Cryst.* B**34**, 3770–3772.
Lindgren, O. (1977). *BLOCK*, a crystallographic least-squares refinement program. Reports from the Department of Inorganic Chemistry, Göteborg 1977: 1.
Mentzen, B. F., Puaux, J.-P. & Sautereau, H. (1978). *Acta Cryst.* B**34**, 1846–1849.
Roof, R. B. Jr (1959). *Phys. Rev.* **113**, 820–825.
Soling, H. (1975). *Acta Chem. Scand. Ser. A*, **29**, 523–527.
Soling, H. (1976). *Acta Chem. Scand. Ser. A*, **30**, 163–170.

Acta Cryst. (1979). B**35**, 2398–2401

Structure of *cis*-Bis(1-methylimidazole)bis(*o*-nitrophenolato)cobalt(II)

By Robert G. Little

Department of Chemistry, University of Maryland Baltimore County, Catonsville, Maryland 21228, *USA*

(*Received* 15 *August* 1978; *accepted* 2 *July* 1979)

Abstract. $C_{20}H_{20}CoN_6O_6$, $[Co(C_4H_6N_2)_2(C_6H_4NO_3)_2]$, monoclinic, $P2_1/c$, a = 13·745 (5), b = 8·010 (2), c = 21·841 (7) Å, β = 114·18 (1)°, Z = 4, D_m = 1·51 (1), D_c = 1·51 Mg m^{-3}. Least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) led to a final, unweighted R value (on F) of 0·040. The Co$^{\rm II}$ ions are octahedrally coordinated to two 1-methylimidazole molecules and two chelated *o*-nitrophenolate ions. The Co—O(phenolic oxygen) bond lengths are 1·972 (2) and 1·978 (2) Å and the Co—O(nitro group) bond lengths are 2·248 (3) and 2·219 (4) Å. The O—Co—O bond angles are 78·4 (1) and 81·3 (1)°. The structure demonstrates the feasibility of metal-ion complexation by nitrated tyrosine residues.

Introduction. In recent years there has been increasing interest in the modification of specific residues in enzymes and proteins so that they will bind lanthanide-ion nuclear-magnetic-resonance shift reagents. These shift reagents can serve as probes of the structures of the proteins in solution. Of particular promise as a modification technique has been the nitration of tyrosine residues. The *o*-nitrophenol portion of a nitrated tyrosine residue is isoelectronic with acetylacetone and it has been suggested that the chelation of metal ions by this group should be facile. Riordan & Sokolovsky (1971) and Riordan & Vallee (1972) have shown that tyrosine residues of a large variety of proteins can be specifically nitrated at the 3-position and thus it appears that chelated lanthanide-ion shift reagents could be widely used in the study of protein structure. Indeed, Marinetti, Snyder & Sykes (1976, 1977) have recently applied this approach to the study of the structure of bovine pancreatic trypsin inhibitor.

Although the use of nitrated tyrosine residues seems plausible there are a number of factors which are troubling. Firstly, it is known that the nitro group is an exceedingly weak Lewis base. Secondly, examination of space-filling models of *o*-nitrophenol suggests that coordination to metal ions should be difficult because the ligand has a relatively small bite. Thirdly, the stability constants of complexes of *o*-nitrophenol or *N*-acetyl-L-3-nitrotyrosine ethyl ester with lanthanide elements have been found to be small and of the order of 10^2 M (Postmus, Magnusson & Craig, 1966; Marinetti, Snyder & Sykes, 1975). Because these factors suggest that the *o*-nitrophenolate group is a poor chelating ligand we decided to determine the structure of a metal complex containing this group in order to establish the nature of the bonding. The structure of *cis*-bis(1-methylimidazole)bis(*o*-nitrophenolato)cobalt(II) reported here unambiguously demonstrates the chelation of metal ions by the nitrophenolate group but also suggests that this group should be a poor ligand toward large metal ions such as the lanthanides.

The complex was prepared by stirring 1·5 g of diaquabis(*o*-nitrophenolato)cobalt(II) with 0·8 ml of 1-methylimidazole in 0·1 litre of CH_2Cl_2 for several hours and then filtering the solution to remove undissolved material. Dark red prisms of the complex were obtained by slow evaporation of the CH_2Cl_2 solution in a refrigerator. Intensity data were collected on a crystal of dimensions 0·60 × 0·36 × 0·30 mm mounted in a thin-walled glass capillary with the crystal's longest dimension (the crystallographic **a** direction) parallel to the capillary walls. The 0·30 mm dimension was perpendicular to the well developed (010) faces; other bounding planes belonged to the {100} and {001}

0567-7408/79/102398-04$01.00

forms. Lattice parameters were obtained by least-squares refinement of the setting angles of 18 reflections with $2\theta \geq 29°$ which had been accurately centered on a Picker four-circle X-ray diffractometer.

For data collection, Mo $K\alpha$ radiation filtered through 3·0 mil ($7{\cdot}6 \times 10^{-2}$ mm) Nb foil was employed. The pulse-height analyzer was set to admit ~95% of the Mo $K\alpha$ peak. Data were collected by the θ–2θ scan method with a symmetric scan range of $\pm 0{\cdot}5°$ in 2θ from the calculated scattering angle. The intensities of all independent reflections with $2\theta \leq 50°$ were measured. The scan rate was 1° min^{-1} and stationary background counts of 10 s were taken at each end of the scan range. Copper-foil attenuators were automatically inserted whenever the count rate exceeded ~10 000 counts s^{-1}. Three standard reflections, chosen to lie in widely separated regions of reciprocal space, were monitored regularly throughout the collection of data. They showed no systematic changes in intensity.

The data were processed using the program *NUFACS* which uses the logic of the program *PICKOUT* previously described by Corfield, Doedens & Ibers (1967) and Doedens & Ibers (1967). The p factor was assigned a value of 0·05. Of the 3280 independent data collected, 3101 were above background by three or more standard deviations. An absorption correction was not applied.

The position of the Co atom was obtained from a sharpened, origin-removed Patterson map calculated with the quantities $|E^2 - 1|$. The structure was refined with anisotropic thermal parameters for all atoms. The H atoms were included as fixed contributions to F_c based upon their 'ideal' positions (methyl C—H = 1·08 Å, aromatic C—H = 0·95 Å). The H atoms of the methyl groups were not located and were not included in the refinement. The final refinement yielded discrepancy factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0{\cdot}040$ and $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0{\cdot}056$. In the last cycle the largest parameter shift was equal to $0{\cdot}5\sigma$.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The final standard deviation of an observation of unit weight was 1·7. Scattering factors for Co, C, N, and O were taken from *International Tables for X-ray Crystallography* (1974) and those of Stewart, Davidson & Simpson (1965) were employed for H. Structure factor calculations included provisions for the real and imaginary parts of the anomalous scattering by the Co atoms. Final atomic positional parameters are listed in Table 1.*

Table 1. *Positional parameters of the atoms in* $C_{20}H_{20}CoN_6O_6$ ($\times 10^4$, *for* Co $\times 10^5$)

Standard deviations are in parentheses.

	x	y	z
Co	−23592 (3)	12833 (5)	2480 (2)
O(1)	−3751 (2)	269 (3)	−318 (1)
O(2)	−1859 (2)	−1233 (3)	22 (1)
O(3)	−1646 (2)	−2882 (4)	−682 (2)
O(4)	−860 (2)	1407 (3)	903 (1)
O(5)	−2540 (2)	148 (3)	1122 (1)
O(6)	−2191 (2)	−879 (4)	2092 (1)
N(1)	−1992 (2)	2266 (4)	−521 (1)
N(2)	−1006 (2)	3408 (3)	−985 (1)
N(3)	−3002 (2)	3459 (3)	448 (1)
N(4)	−3889 (2)	5210 (3)	802 (1)
N(5)	−2217 (2)	−1891 (4)	−547 (2)
N(6)	−1876 (2)	−339 (3)	1680 (1)
C(1)	−1011 (3)	2639 (5)	−440 (2)
C(2)	−2043 (3)	3515 (5)	−1441 (2)
C(3)	−2632 (3)	2828 (5)	−1144 (2)
C(4)	−70 (3)	4034 (6)	−1073 (2)
C(5)	−3649 (3)	3607 (4)	747 (2)
C(6)	−3359 (3)	6139 (4)	519 (2)
C(7)	−2814 (3)	5059 (4)	305 (2)
C(8)	−4571 (4)	5820 (6)	1126 (2)
C(9)	−3982 (3)	−556 (4)	−867 (2)
C(10)	−5040 (3)	−492 (5)	−1364 (2)
C(11)	−5333 (4)	−1285 (6)	−1967 (2)
C(12)	−4591 (5)	−2209 (7)	−2116 (2)
C(13)	−3585 (4)	−2369 (5)	−1649 (2)
C(14)	−3266 (3)	−1573 (4)	−1019 (2)
C(15)	−333 (2)	583 (3)	1443 (1)
C(16)	799 (2)	571 (4)	1691 (2)
C(17)	1425 (3)	−195 (5)	2287 (2)
C(18)	981 (3)	−1029 (5)	2666 (2)
C(19)	−99 (3)	−1067 (4)	2449 (2)
C(20)	−760 (2)	−282 (3)	1845 (1)
H1C(1)	−389	2395	−49
H1C(2)	−2296	3978	−1878
H1C(3)	−3388	2748	−1341
H1C(5)	−3917	2691	907
H1C(6)	−3369	7320	480
H1C(7)	−2367	5362	88
H1C(13)	−3086	−3025	−1738
H1C(12)	−4794	−2715	−2542
H1C(11)	−6050	−1208	−2289
H1C(10)	−5561	119	−1277
H1C(16)	1132	1104	1440
H1C(17)	2179	−151	2442
H1C(18)	1425	−1565	3072
H1C(19)	−410	−1627	2706

Discussion. The crystal structure consists of discrete molecules of $C_{20}H_{20}CoN_6O_6$. The numbering scheme used in this paper and a general view of the complex are shown in Fig. 1. The figure also shows the averaged bond lengths and some bond angles in the complex.

The coordination geometry about the Co atom is *cis*-octahedral and the complex has pseudo-C_2 symmetry. The *o*-nitrophenolate ions are coordinated in a chelating fashion such that the coordinated nitro groups are *cis*.

---

* Lists of structure factors, thermal parameters, r.m.s. amplitudes of thermal vibration, and least-squares planes and interplanar angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34569 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

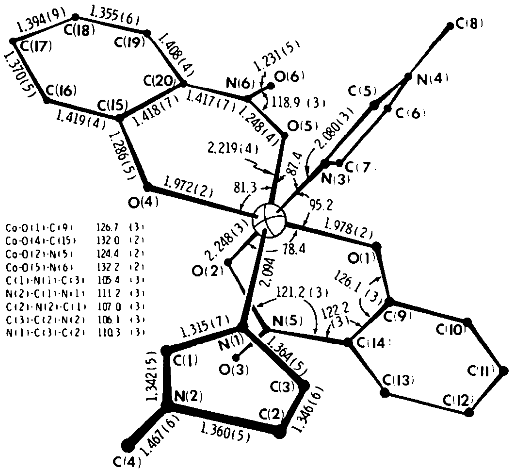
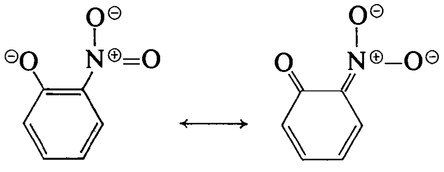


Fig. 1. Drawing of the complex $C_{20}H_{20}CoN_6O_6$ showing the numbering scheme and the averaged bond lengths (Å), where appropriate, and some bond angles (°). The H atoms have been omitted for clarity. The values in parentheses are the larger of either the standard deviation in the mean value or the individual measurement. E.s.d.'s for O—Co—O and O—Co—N are 0·1 °.

The coordination polyhedron is significantly distorted from regular octahedral. As shown in Fig. 1, the bond angles about the Co range from 78·4 to 98·2° and the Co atom is not coplanar with any four of the six ligating atoms.

The lengths of the bonds from Co to the phenolic O atoms average 1·975 (3) Å. This is somewhat shorter than the Co—O bond length of 2·034 (3) Å found in *trans*-Co(acac)$_2$(py)$_2$ (Elder, 1968) and shorter than the 2·055 (30) Å found in tetrameric Co(acac)$_2$ (Cotton & Elder, 1965). The Co—N bond lengths in the present complex average 2·087 (7) Å. This compares well with the 2·05 Å expected for a N(sp^2)—Co^{II} bond (Little & Ibers, 1974). The two bonds to Co involving the nitro-group oxygen atoms are 2·248 (3) and 2·219 (4) Å. The chemical non-equivalence of the two *o*-nitrophenolate groups suggested by these bond lengths is further demonstrated by the geometry of the two ligands. Each *o*-nitrophenolate group is non-planar. The nitro groups are rotated by 7·3 and 9·4 ° from the planes of the phenyl rings containing carbon atoms C(9)–C(14) and C(15)–C(20) respectively.

The phenyl rings of the chelated *o*-nitrophenolate ions are strictly planar and the average C–C bond length in these two rings is 1·394 Å with a standard deviation of 0·024 Å. This deviation is four times the standard deviation of an individual C–C bond length and suggests that an apparent shortening of two bonds in each phenyl ring is real. Such a shortening is consistent with a resonance structure which involves delocalization of electron density from the phenolic O on to the nitro group, as shown below.



Similar variations in C–C distances have been observed in two K salts of *o*-nitrophenol (Krough Anderson & Krough Anderson, 1975; Bush & Truter, 1971). In each case a shortening of the C(3)–C(4) and C(5)–C(6) distances was observed.

The bond lengths associated with the nitro groups and the phenolic O atoms also suggest such delocalization. The N—C bond lengths average 1·417 (7) Å, which is significantly shorter than the N—C bond lengths found in *p*-nitrophenol (Coppens & Schmidt, 1965), *m*-nitrophenol (Pandarese, Ungaretti & Coda, 1975), *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961) and *N*,*N*-dimethyl-3-nitroaniline (Delugeard & Messager, 1975).

The phenolic C—O bond lengths in the complex average 1·286 (5) Å. This may be compared to the C—O bond lengths of 1·352 (2) and 1·366 (3) Å observed in *p*-nitro- and *m*-nitrophenol respectively (Coppens & Schmidt, 1965; Pandarese, Ungaretti & Coda, 1975). Again, a significant shortening due to delocalization is evident. Very little change in the N—O bond lengths is apparent.

The *o*-nitrophenolate group is isoelectronic with the acetylacetonate ion but, as the present structure shows, the bite of the *o*-nitrophenolate group is much smaller than that of the acetylacetonate ion. In *trans*-Co(acac)$_2$(py)$_2$ (Elder, 1968) and in tetrameric Co(acac)$_2$ (Cotton & Elder, 1965) the O—Co—O bond angles range from 89·8 to 97·3° whereas in the present complex they are 78·4 (10) and 81·3 (9)°.

The smaller bite of the *o*-nitrophenolate group is consistent with it being a weaker ligand than the acetylacetonate ion and suggests that chelation of relatively large metal ions such as the lanthanides by *o*-nitrophenol may be unfavorable.

References

Bush, M. A. & Truter, M. R. (1971). *J. Chem. Soc. A*, pp. 745–750.

Coppens, P. & Schmidt, G. M. J. (1965). *Acta Cryst.* **18**, 654–663.

Corfield, P. W. R., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

Cotton, F. A. & Elder, R. C. (1965). *Inorg. Chem.* **4**, 1145–1151.

Delugeard, Y. & Messager, J. C. (1975). *Acta Cryst.* B**31**, 2809–2813.

Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 204–210.

Elder, R. C. (1968). *Inorg. Chem.* **7**, 1117–1123.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–97. Birmingham: Kynoch Press.
Krough Anderson, E. & Krough Anderson, I. G. (1975). *Acta Cryst.* B**31**, 391–393.
Little, R. G. & Ibers, J. A. (1974). *J. Am. Chem. Soc.* **96**, 4440–4446.
Marinetti, T. D., Snyder, G. H. & Sykes, B. D. (1975). *J. Am. Chem. Soc.* **97**, 6562–6570.
Marinetti, T. D., Snyder, G. H. & Sykes, B. D. (1976). *Biochemistry*, **15**, 4600–4608.
Marinetti, T. D., Snyder, G. H. & Sykes, B. D. (1977). *Biochemistry*, **16**, 647–653.
Pandarese, F., Ungaretti, L. & Coda, A. (1975). *Acta Cryst.* B**31**, 2671–2675.
Postmus, C., Magnusson, L. B. & Craig, C. A. (1966). *Inorg. Chem.* **5**, 1154–1157.
Riordan, J. F. & Sokolovsky, M. (1971). *Acc. Chem. Res.* **4**, 353–360.
Riordan, J. F. & Vallee, B. L. (1972). *Methods Enzymol.* **25**, 515–521.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Trueblood, K. N., Goldish, E. & Donohue, J. (1961). *Acta Cryst.* **14**, 1009–1012.

Acta Cryst. (1979). B**35**, 2401–2403

Aqua(cyclobutane-1,1-dicarboxylato)(*N,N,N′,N′*-tetramethylethylenediamine)copper(II) Monohydrate

By Aarne Pajunen and Seija Pajunen

Department of Inorganic Chemistry, University of Helsinki, Vuorikatu 20, *SF*-00100 *Helsinki* 10, *Finland*

(*Received* 21 *May* 1979; *accepted* 3 *July* 1979)

Abstract. $[Cu(C_6H_{16}N_2)(C_6H_6O_4)(H_2O)].H_2O$, $C_{12}H_{24}CuN_2O_5.H_2O$, monoclinic, $P2_1$, $a = 9·354$ (4), $b = 8·525$ (3), $c = 10·363$ (8) Å, $\beta = 102·02$ (5)°, $Z = 2$. The structure was refined to $R = 0·032$ for 1330 unique reflections. The coordination polyhedron is square-pyramidal, with the base formed by two N atoms of the diamine and two O atoms of the dicarboxylic acid. The apex of the pyramid is occupied by a water O atom.

Introduction. The title compound was prepared from copper(II) carbonate, cyclobutane-1,1-dicarboxylic acid and *N,N,N′,N′*-tetramethylethylenediamine (molar ratio 1:1:1) in a water–methanol mixture. The cell parameters and intensities were measured on a Syntex $P2_1$ diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å). Systematic absences $0k0$ with k odd indicated space group $P2_1$ or $P2_1/m$. The noncentrosymmetric $P2_1$ was suggested by normalized structure factor statistics. Intensities for 1609 unique reflections in the range $3 < 2\theta < 55°$ were collected by the ω-scan technique.

The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1978) and refined by full-matrix least squares with experimental weights $w = 4F_o^2/\sigma_I^2$. Only the 1330 most significant reflections [$I > 3\sigma(I)$] were used in the refinement. The positions of the H atoms were deduced partly from a difference synthesis and partly from chemical considerations. The H atoms were included in the refinement with fixed isotropic temperature parameters ($U = 0·06$ Å^2) and fixed positional coordinates. The final R was 0·032.* Scattering factors for the non-hydrogen atoms and the H atoms were taken from Cromer &

Table 1. *Fractional atomic coordinates* (×10^4) *of the non-hydrogen atoms*

	x	*y*	*z*
Cu	3436 (1)	5000	3286 (1)
O(1)	4827 (13)	3448 (12)	3125 (10)
O(2)	6884 (12)	2640 (14)	2552 (12)
O(3)	4845 (12)	6731 (12)	3153 (10)
O(4)	6842 (14)	7509 (12)	2558 (11)
O(5)	4132 (4)	5004 (16)	5574 (3)
O(6)	1322 (5)	5084 (22)	7745 (8)
N(1)	1855 (13)	3400 (13)	3073 (12)
N(2)	1729 (13)	6672 (15)	3092 (12)
C(1)	5828 (5)	4939 (20)	1659 (4)
C(2)	4476 (5)	5081 (25)	446 (4)
C(3)	5528 (6)	4987 (29)	−480 (5)
C(4)	6843 (6)	4971 (30)	651 (5)
C(5)	5820 (13)	3563 (11)	2525 (11)
C(6)	5932 (14)	6495 (17)	2486 (12)
C(7)	395 (9)	4203 (13)	2733 (9)
C(8)	498 (8)	5728 (12)	3438 (9)
C(9)	1575 (23)	2613 (28)	1803 (18)
C(10)	2036 (22)	2196 (22)	4074 (19)
C(11)	1683 (23)	7600 (27)	1885 (17)
C(12)	2027 (21)	7767 (19)	4258 (17)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34577 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/79/102401-03$01.00