

Ähnliche Bindungsverhältnisse weist das 1-Methylcytosin-silber(I)-nitrat auf (Kistenmacher, Rossi & Marzilli, 1979): 4-fach koordiniertes Silber(I) mit einem Winkel O—Ag—N im 8-Ring von 136,2° sowie ein brückenbindendes Sauerstoffatom, welches die 8-Ringe zu hochmolekularen Ketten miteinander verknüpft.

Die Ag—O- bzw. Ag—N-Abstände [2,23 (1)–2,53 (1) Å] in BPAg (Tabelle 2) sind erwartungsgemäss länger als die in Silber(I) komplexen mit linearer Ag-Anordnung gefundenen Werte, die dort weniger als 2,20 Å betragen (z.B. Acland & Freeman, 1971; Menchetti, Rossi & Tazzoli, 1970). Besonders lang ist die Bindung Ag—O(1'), welche die Verknüpfung zweier benachbarter 8-Ringe bewirkt.

Die Struktur des (Benzoato)-(pyridin)-iod(I) (Hartl & Hedrich, 1981) besitzt mit der hier beschriebenen Silberverbindung wenig Gemeinsamkeiten, da sie monomer in Form von gestreckten Molekülen (Winkel N—I—O 176,7 bzw. 175,7°) vorliegt und das zentrale I^I die Koordinationszahl 2 betätigt. Diese Unterschiede in den Strukturen sind in den Schwingungsspektren dieser Verbindungen deutlich zu erkennen. Die Bandenlagen im Bereich von 1200–1700 cm⁻¹ lassen darauf schliessen, dass in BPAg beide Carboxylat-Sauerstoffatome zur Koordination herangezogen werden, in der formelanalogen Iod(I)-Verbindung dagegen nur eins (Hedrich, 1977).

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Literatur

- ACLAND, C. B. & FREEMAN, H. C. (1971). *Chem. Commun.* pp. 1016–1017.
 BLAKESLEE, A. E. & HOARD, J. L. (1956). *J. Am. Chem. Soc.* **78**, 3029–3033.
 BLUES, E. T., DREW, M. G. B. & FEMI-ONADEKO, B. (1977). *Acta Cryst.* **B33**, 3965–3967.
 BURNHAM, C. W. (1966). *Am. Mineral.* **51**, 159–164.
 CHARBONNIER, F., FAURE, R. & LOISELEUR, H. (1981). *Rev. Chim. Minér.* **18**(3), 245–253.
 COREY, R. B. & WYCKOFF, R. W. G. (1934). *Z. Kristallogr.* **87**, 264–274.
 DREW, M. G. B., EDWARDS, D. A. & RICHARDS, R. (1973). *Chem. Commun.* pp. 124–125.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A 27**, 368–376.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 HARTL, H. & HEDRICH, M. (1981). *Z. Naturforsch. Teil B*, **36**, 922–928.
 HEDRICH, M. (1977). *Synthese von Iodonium- und Silberverbindungen und deren Untersuchung mit Methoden der Röntgenbeugung und Schwingungsspektroskopie*. Diplomarbeit. Freie Univ. Berlin.
 HUNT, G. W., LEE, T. C. & AMMA, E. L. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 909–913.
 IGNATEVA, E. M. & KHARITONOVA, R. I. (1969). *Ref. Zh. Khim.* Abstr. No. 16V52.
International Tables for X-ray Crystallography (1968). Bd III, S. 202–203, 206–207, 216. Birmingham: Kynoch Press.
 KISTENMACHER, T. J., ROSSI, M. & MARZILLI, L. G. (1979). *Inorg. Chem.* **18**, 240–244.
 MENCHETTI, S., ROSSI, G. & TAZZOLI, V. (1970). *Rend. Ist. Lomb. Sci. Lett. Cl. Sci. Mat. Nat.* **A104**, 309–316.
 MOUNTS, R. D., OGURA, T. & FERNANDO, Q. (1974). *Inorg. Chem.* **13**, 802–805.
 PEARSON, R. G. (1963). *J. Am. Chem. Soc.* **85**, 3533–3539.
 RAO, J. K. M. & VISWAMITRA, M. A. (1972). *Acta Cryst.* **B28**, 1484–1496.
 STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Bis(2-amino-2-methyl-1-propanol)bis(*o*-nitrobenzoato-*O*)copper(II), [Cu(C₄H₁₁NO)₂(C₇H₄NO₂)₂]

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Abstract. $M_r = 574.1$, orthorhombic, $Pna2_1$, $a = 10.933$ (3), $b = 23.188$ (9), $c = 9.921$ (2) Å, $V = 2529$ (1) Å³, $Z = 4$, $D_m = 1.52$, $D_x = 1.51$ Mg m⁻³, graphite-monochromatized Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.96$ mm⁻¹, $F(000) = 1196$, $T = 298$ K, $R = 0.036$, $R_w = 0.041$ for 2141 observed reflections. The coordination geometry around the Cu atom is distorted

octahedral comprising two O atoms from the two monodentate carboxylate groups and the two N atoms from the two aminoalcohol molecules in the equatorial plane, and the two O atoms of the aminoalcohols above and below this plane at distances of 2.423 (4) and 2.479 (4) Å from the Cu. Very different interplanar-angle values exist for the same substituent in the two

o-nitrobenzoate ligands. However, in each ligand the twisting of one of the two substituents depends on the other in such a manner that the sum of the dihedral angles between the benzene and the substituent planes is retained at approximately 90°. Weak hydrogen bonds link the monomeric complex into a chain in the *a* direction.

Introduction. The overcrowding between vicinal bulky substituents linked to a rigid aromatic ring manifests itself as twisting of the substituents from the benzene plane. Large deviations of nitro groups from the benzene plane have been reported in aromatic nitroorganics, for example: 2,4,6-trinitroaniline (Holden, Dickinson & Bock, 1972), 2,3,4,6-tetranitroaniline (Dickinson, Stewart & Holden, 1966) and 3,5-diamino-2,4,6-trinitrophenol (Bhattacharjee & Ammon, 1981) where dihedral angles up to 64° exist. The effect of overcrowding is also clearly seen in mononitrobenzoic acids. Whereas the dihedral angles between the planes of the substituents and the plane of the ring are in the range 1.6–6.0 and 1.3–21.7° for the COO⁻ and NO₂ groups in *p*- and *m*-nitrobenzoic acids (Colapietro & Domenicano, 1977; Dhaneshwar, Tavale & Pant, 1974; Dhaneshwar, Kulkarni, Tavale & Pant, 1975), the corresponding angles in *o*-nitrobenzoic acid are 24.1 and 54.3° (Tavale & Pant, 1973). The magnitude of the dihedral angle depends on factors such as intra- and intermolecular contacts and hydrogen bonds in which the substituents participate, coordination of the substituents in coordination compounds, charges within the substituents and, in the case of a nitro substituent (dipolar group), on increased double-bond character of the C–N bond as a result of π -electron delocalization from the aromatic ring to the nitro group (Bhattacharjee & Ammon, 1981).

Studies on mixed-ligand Cu^{II} complexes formed by 1,3-propanediamine and different halogen-substituted benzoates have shown that crystals containing *o*-halobenzoates are difficult to obtain (Orama, 1976). Of two reported Cu^{II} complexes containing a nitrobenzoate ligand, one has 1,3-propanediamine and *p*-nitrobenzoate as ligands (Klinga, 1976) and the other 1,3-propanediamine and *m*-nitrobenzoate (Klinga, 1979). In this work we investigate the effect of the nitro group on the coordination of the aminoalcohol and the carboxylate group to the Cu^{II} ion, when the nitro group is in the *ortho* position. The aryl carboxylate compounds formed by copper(II) benzoate and copper(II) salicylate with 2-amino-2-methyl-1-propanol have been described earlier (Muhonen & Hämäläinen, 1978; Muhonen, 1982).

Experimental. Copper(II) *o*-nitrobenzoate prepared in finely powdered form as described by Orama, Huttner, Lorenz, Marsili & Frank (1976) for copper(II) *m*-bromobenzoate, crude product of the title compound

precipitated from an ethanol solution of copper(II) *o*-nitrobenzoate, which was used without prior analysis, and 2-amino-2-methyl-1-propanol (molar ratio 1:2), with the solvent allowed to evaporate; crystallization from a mixture of 1- and 2-propanol yielded green crystals, which gradually decomposed in air. Density by flotation in a mixture of chloroform and carbon tetrachloride, Nicolet P3 diffractometer, 0.60 × 0.50 × 0.15 mm, coated with epoxy glue, ω -scan technique, variable scan rate, 1.7 to 29.3° min⁻¹, 3476 independent reflections in the range $4 < 2\theta < 56^\circ$, 2141 with $|F_o| > 5\sigma(|F_o|)$; two test reflections checked after every 98 intensity measurements showed no decomposition of crystal; Lorentz, polarization and empirical absorption corrections applied; ψ scans over five reflections, evenly distributed over the 2θ range, showed 20–25% decrease in intensities as the crystal was rotated from the least to the most absorbing position.

Systematic absences suggested two possible space groups: the non-centrosymmetric *Pna2*₁ and the centrosymmetric *Pnam*, an alternative orientation of *Pnma*. The position of the Cu atom was found from a sharpened Patterson vector map, assuming four molecules per unit cell. The value of 0.25 obtained for the *z* coordinate (*y* in non-centrosymmetric space group) would demand that the Cu atom be located on the mirror plane in the centrosymmetric space group. This demand being considered chemically too stringent, the space group *Pnam* was rejected. The choice of *Pna2*₁ was confirmed by the geometry of the complex molecule. The increased symmetry of the electron-density map calculated with phases derived from the Cu-atom position alone (*y* ~ 0.25) led to a few trials in which some of the highest peaks in the environment of Cu were included. The iterative process to include more atoms together with Fourier refinement led to gradual convergence. Final refinement (on *F*) carried out by full-matrix least squares; Univac 1108 computer, XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), scattering factors from program system, anomalous-dispersion correction for the scattering factor for Cu from *International Tables for X-ray Crystallography* (1974), coordinates of H atoms from a difference map (at *R* = 0.048) and allowed to vary initially, H atoms included in the last few cycles with fixed coordinates from the previous refinement, with fixed $U_{\text{iso}} 0.05 \text{ \AA}^2$, $w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$, anisotropic for non-hydrogen atoms, *R* = 0.036, *R_w* = 0.041.*

Discussion. Final atomic parameters are given in Table 1, and bond lengths and angles in Table 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38320 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and U_{eq} values ($\times 10^2$) for non-H atoms

	x	y	z	$U_{eq}(\text{\AA}^2)$
Cu	4795.2 (4)	2550.5 (2)	5000.0	2.63 (3)
O(1)	3282 (3)	2192 (2)	3435 (4)	4.2 (2)
O(2)	6399 (3)	2868 (2)	6592 (4)	4.9 (2)
O(3)	4747 (3)	3294 (1)	3944 (4)	3.5 (2)
O(4)	2903 (3)	3644 (2)	4458 (4)	4.6 (2)
O(5)	6879 (3)	3934 (2)	2941 (5)	5.8 (2)
O(6)	6162 (4)	3373 (2)	1411 (4)	5.1 (2)
O(7)	5058 (3)	1820 (1)	6067 (4)	3.9 (2)
O(8)	3294 (3)	1335 (2)	6101 (5)	5.2 (2)
O(9)	3356 (4)	1520 (2)	8965 (5)	6.1 (3)
O(10)	2832 (4)	686 (2)	9706 (6)	9.6 (4)
N(1)	5841 (3)	2211 (2)	3568 (4)	2.9 (2)
N(2)	3811 (3)	2876 (2)	6529 (4)	3.1 (2)
N(3)	6110 (4)	3794 (2)	2122 (4)	3.5 (2)
N(4)	3500 (4)	1004 (2)	9075 (5)	4.5 (3)
C(1)	3988 (5)	2161 (2)	2239 (6)	3.8 (3)
C(2)	5225 (4)	1887 (2)	2478 (5)	3.0 (2)
C(3)	5054 (4)	1255 (2)	2913 (6)	3.9 (3)
C(4)	5989 (6)	1902 (2)	1186 (6)	5.0 (3)
C(5)	5715 (6)	2863 (3)	7830 (6)	5.0 (4)
C(6)	4487 (5)	3169 (2)	7632 (5)	3.5 (3)
C(7)	4699 (6)	3794 (3)	7243 (8)	6.1 (4)
C(8)	3750 (6)	3139 (3)	8953 (8)	6.7 (4)
C(9)	3883 (4)	3654 (2)	3844 (5)	2.7 (2)
C(10)	4062 (4)	4140 (2)	2820 (5)	2.8 (2)
C(11)	5034 (4)	4186 (2)	1980 (5)	3.1 (2)
C(12)	5122 (5)	4587 (2)	945 (6)	4.0 (3)
C(13)	4189 (5)	4979 (2)	799 (7)	4.7 (3)
C(14)	3211 (5)	4965 (2)	1654 (7)	5.0 (3)
C(15)	3148 (5)	4545 (2)	2656 (6)	3.8 (3)
C(16)	4381 (4)	1413 (2)	6409 (5)	3.2 (2)
C(17)	5011 (4)	955 (2)	7258 (5)	2.9 (2)
C(18)	4586 (4)	739 (2)	8458 (5)	3.6 (3)
C(19)	5157 (5)	302 (2)	9145 (6)	4.7 (3)
C(20)	6202 (5)	65 (2)	8624 (7)	5.0 (3)
C(21)	6652 (5)	267 (3)	7458 (8)	4.8 (3)
C(22)	6095 (5)	719 (2)	6749 (6)	3.8 (3)

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Table 2 (cont.)

Cu—O(3)—C(9)	128.5 (3)	Cu—O(7)—C(16)	133.7 (3)
O(3)—C(9)—O(4)	126.9 (5)	O(7)—C(16)—O(8)	127.9 (5)
O(3)—C(9)—C(10)	116.1 (4)	O(7)—C(16)—C(17)	114.0 (4)
O(4)—C(9)—C(10)	116.9 (4)	O(8)—C(16)—C(17)	118.1 (4)
C(9)—C(10)—C(11)	124.5 (4)	C(16)—C(17)—C(18)	125.4 (4)
C(9)—C(10)—C(15)	118.9 (4)	C(16)—C(17)—C(22)	117.3 (4)
O(5)—N(3)—O(6)	125.0 (5)	O(9)—N(4)—O(10)	124.5 (5)
O(5)—N(3)—C(11)	116.7 (4)	O(9)—N(4)—C(18)	118.6 (4)
O(6)—N(3)—C(11)	118.3 (4)	O(10)—N(4)—C(18)	116.7 (4)
N(3)—C(11)—C(10)	121.0 (4)	N(4)—C(18)—C(17)	118.9 (4)
N(3)—C(11)—C(12)	114.9 (4)	N(4)—C(18)—C(19)	118.1 (4)
C(10)—C(11)—C(12)	124.1 (4)	C(17)—C(18)—C(19)	122.9 (4)
C(11)—C(12)—C(13)	117.9 (5)	C(18)—C(19)—C(20)	119.4 (5)
C(12)—C(13)—C(14)	120.2 (5)	C(19)—C(20)—C(21)	119.5 (5)
C(13)—C(14)—C(15)	119.8 (5)	C(20)—C(21)—C(22)	122.1 (5)
C(14)—C(15)—C(10)	121.4 (5)	C(21)—C(22)—C(17)	118.7 (5)
C(15)—C(10)—C(11)	116.4 (4)	C(22)—C(17)—C(18)	117.2 (4)

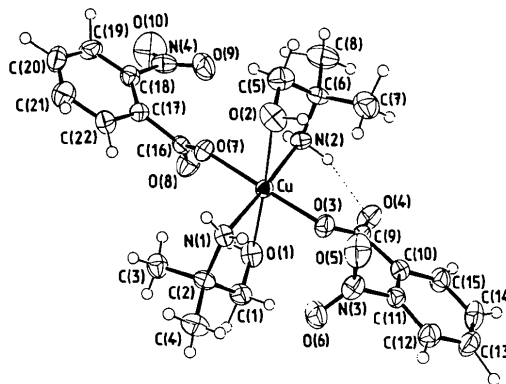


Fig. 1. A view of the molecule. Atoms are drawn with 50% probability thermal ellipsoids.

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

Cu—N(1)	1.990 (4)	Cu—N(2)	2.010 (4)
Cu—O(3)	2.018 (3)	Cu—O(7)	2.018 (3)
Cu—O(1)	2.423 (4)	Cu—O(2)	2.479 (4)
C(1)—O(1)	1.420 (7)	C(5)—O(2)	1.440 (7)
C(1)—C(2)	1.520 (7)	C(5)—C(6)	1.538 (8)
C(2)—N(1)	1.481 (6)	C(6)—N(2)	1.487 (6)
C(2)—C(3)	1.539 (7)	C(6)—C(7)	1.518 (8)
C(2)—C(4)	1.533 (8)	C(6)—C(8)	1.542 (9)
C(9)—O(3)	1.268 (5)	C(16)—O(7)	1.249 (5)
C(9)—O(4)	1.238 (6)	C(16)—O(8)	1.247 (6)
C(9)—C(10)	1.530 (7)	C(16)—C(17)	1.522 (7)
N(3)—O(5)	1.217 (6)	N(4)—O(9)	1.212 (7)
N(3)—O(6)	1.206 (6)	N(4)—O(10)	1.214 (7)
N(3)—C(11)	1.498 (6)	N(4)—C(18)	1.476 (6)
C(10)—C(11)	1.359 (6)	C(17)—C(18)	1.373 (7)
C(11)—C(12)	1.389 (7)	C(18)—C(19)	1.373 (7)
C(12)—C(13)	1.378 (7)	C(19)—C(20)	1.374 (8)
C(13)—C(14)	1.370 (9)	C(20)—C(21)	1.342 (10)
C(14)—C(15)	1.393 (8)	C(21)—C(22)	1.403 (9)
C(15)—C(10)	1.385 (7)	C(22)—C(17)	1.405 (7)
N(1)—Cu—O(3)	89.0 (2)	N(2)—Cu—O(7)	89.8 (2)
N(1)—Cu—O(7)	87.7 (2)	N(2)—Cu—O(3)	93.2 (2)
N(1)—Cu—O(1)	78.7 (1)	N(2)—Cu—O(2)	77.9 (1)
N(1)—Cu—O(2)	99.3 (1)	N(2)—Cu—O(1)	104.0 (1)
N(1)—Cu—N(2)	176.5 (1)	O(3)—Cu—O(7)	173.2 (1)
O(1)—Cu—O(3)	86.7 (1)	O(2)—Cu—O(7)	79.2 (1)
O(1)—Cu—O(7)	98.4 (1)	O(2)—Cu—O(3)	95.5 (1)
O(1)—Cu—O(2)	177.0 (1)		
Cu—N(1)—C(2)	117.2 (2)	Cu—N(2)—C(6)	117.2 (3)
Cu—O(1)—C(1)	100.2 (3)	Cu—O(2)—C(5)	99.8 (3)
O(1)—C(1)—C(2)	112.3 (4)	O(2)—C(5)—C(6)	110.2 (5)
N(1)—C(2)—C(1)	108.1 (4)	N(2)—C(6)—C(5)	108.8 (4)
N(1)—C(2)—C(3)	109.5 (4)	N(2)—C(6)—C(7)	109.0 (4)
N(1)—C(2)—C(4)	110.4 (4)	N(2)—C(6)—C(8)	110.0 (4)
C(1)—C(2)—C(3)	109.4 (4)	C(5)—C(6)—C(7)	109.8 (5)
C(1)—C(2)—C(4)	110.5 (4)	C(5)—C(6)—C(8)	109.4 (4)
C(3)—C(2)—C(4)	108.8 (4)	C(7)—C(6)—C(8)	109.9 (5)

The six-coordinate monomeric complex is shown in Fig. 1. The Cu atom lies nearly in the equatorial plane, with a shift toward the O(1) atom of 0.074 (2) Å. The plane itself is slightly tetrahedrally distorted, the r.m.s. distance of the four plane-determining atoms from the plane being 0.031 (4) Å. The complex is the first 2-amino-2-methyl-1-propanol complex composed of monomeric units to have the aminoalcohol O atom in the axial position. The axial Cu—O bond lengths and the angles these bonds make with the normal of the equatorial plane are 2.423 (4) Å and 14.0 (1)° for the Cu—O(1) bond and 2.479 (4) Å and 13.4 (1)° for the Cu—O(2) bond. The aminoalcohol ligands, and to a lesser extent the aromatic six-membered rings, are in nearly centrosymmetric arrangement around the Cu atom. The deviations from the centrosymmetry vary between 0.12 (1) and 0.26 (1) Å for the non-hydrogen atoms of the aminoalcohol ligand and between 0.57 (1) and 1.05 (1) Å for the C atoms of the aromatic ring. The position of the substituents relative to the Cu atom renders the molecule decisively internally non-centrosymmetric: the carboxylate groups are in *cis* configuration not *trans* and the nitro groups are unsymmetrically positioned in the *z* direction. The five-membered aminoalcohol chelate rings have torsion angles O(1)—C(1)—C(2)—N(1) and O(2)—C(5)—C(6)

—N(2) of $-55.0(5)$ and $57.7(6)^\circ$, respectively, indicative of *gauche* conformations. The C(1) and C(2) atoms of the first chelate ring deviate $0.512(6)$ and $-0.147(6)$ Å from the N(1)—Cu—O(1) plane, and the C(5) and C(6) atoms of the second ring deviate $-0.559(7)$ and $0.145(6)$ Å from the N(2)—Cu—O(2) plane.

The roles of the benzoate, salicylate and *o*-nitrobenzoate ions in Cu^{II} complexes formed with 2-amino-2-methyl-1-propanol are different. In the benzoate compound (Muhonen & Hämäläinen, 1978) the carboxylate ion does not take part in coordination. In the salicylate complex (Muhonen, 1982) the salicylate ligands coordinate to a different Cu atom from the aminoalcohol ligands, interacting weakly through one of the carboxylate O atoms at the long axial distance of $2.658(4)$ Å with the Cu atom coordinated by the aminoalcohol ligands. In the present complex the *o*-nitrobenzoate ligands are firmly bound to the same Cu atom as the aminoalcohols. Both *o*-nitrobenzoate ligands coordinate through one of the carboxylate O atoms, one ligand through the carboxylate O on the side of the NO₂ group and the other through that on the opposite side to the NO₂ group.

Table 3 shows the dihedral angles between the planes of the substituents and the plane of the benzene ring, and the means of the absolute values of the four acute angles describing the rotation of substituents. Very different interplanar-angle values exist for the same substituent in the two *o*-nitrobenzoate ligands. Comparison of the mean rotation angles of the substituents with the dihedral angles shows that rotation of the substituents about the C—C or the C—N bond is the main reason for the twisting, except for the carboxylate group C(9)O(3)O(4)⁻, which is more bent out of the plane than rotated.

The contribution of π -electron delocalization from the aromatic ring to the nitro group can be determined through the correlation of the C—N distance with the nitro-group rotation. Delocalization requires decrease of rotation about the C—N bond with decrease in the bond length (Bhattacharjee & Ammon, 1981). This relationship is found for both the *o*-nitrobenzoate ligands as well as for the *o*-nitrobenzoic acid. The attachment of the carboxylate groups to the metal ion evidently establishes the twisting of these groups in the first place. The hydrogen bonding, another factor tending to orient the substituents, is weak throughout the structure and is different for the two *o*-nitrobenzoate ligands (Fig. 2 and Table 4). The variety of magnitudes for dihedral angles between the benzene and the substituent planes and the closeness of the values of these angles to those for rotation of the substituents about the C—C or C—N bond suggest a shallow rotation-energy well for the rotations of the substituents in the *o*-nitrobenzoate ligands and *o*-nitrobenzoic acid. Rotation of one of the two substituents depends on the other, because the sum of

the mean rotation angles (and the dihedral angles) is always approximately 90° .

The effects of substituents on the geometry of aromatic six-membered rings have been quantitatively analyzed by Domenicano & Murray-Rust (1979) and Norrestam & Schepper (1981). The latter, not confining themselves to mono and *para*-disubstituted derivatives, derived deformation parameters for both the endocyclic angles and bond distances of the ring, utilizing a wider range of multisubstituted organic benzene derivatives.

Table 3. Dihedral angles ($^\circ$) between least-squares planes, and angles ($^\circ$) of mean rotation for substituents

Planes			
I [C(10)—C(15)],*		II [C(9), O(3), O(4)],	
IV [C(17)—C(22)],*		V [C(16), O(7), O(8)],	
		III [N(3), O(5), O(6)],	
		VI [N(4), O(9), O(10)]	
Dihedral angles			
Planes	Angle	Planes	Angle
I, II	8.0 (6)	IV, V	53.1 (5)
I, III	83.9 (3)	IV, VI	35.6 (7)
II, III	88.1 (4)	V, VI	54.4 (6)
I, IV	9.0 (10)		
Mean rotations†			
O(3)/O(4)—C(9)—C(10)—C(11)/C(15)		2.9 (3)	
O(7)/O(8)—C(16)—C(17)—C(18)/C(22)		52.4 (3)	
O(5)/O(6)—N(3)—C(11)—C(10)/C(12)		83.9 (3)	
O(9)/O(10)—N(4)—C(18)—C(17)/C(19)		35.6 (3)	

* R.m.s. deviations of atoms defining the planes I and IV are 0.012 (5) and 0.007 (5) respectively.

† See text.

Table 4. Hydrogen-bond distances and angles

D—H...A	Angle ($^\circ$)	D...A (Å)	H...A (Å)*	D—H (Å)*
N(1)—H(10)...O(4)	156	3.138 (6)	2.44	0.74
N(1)—H(11)...O(1)	142	3.022 (5)	2.32	0.83
N(2)—H(21)...O(4)	148	2.896 (6)	2.00	0.99
N(2)—H(22)...O(2)	151	3.164 (5)	2.49	0.73
O(1)—H(1)...O(5)	125	3.072 (5)	2.57	0.76
O(2)—H(12)...O(8)	139	2.827 (6)	2.00	0.98

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, z$.

* E.s.d.'s obtained prior to the final cycles were approximately 0.07 Å.

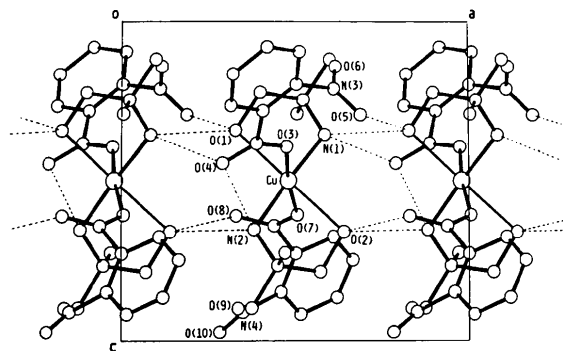


Fig. 2. Projection of a chain along *b*. The molecules with symmetry codes $-\frac{1}{2}+x, \frac{1}{2}-y, z$; x, y, z ; $\frac{1}{2}+x, \frac{1}{2}-y, z$ are drawn.

The distortions are shown to be more significant for the endocyclic angles than for the bond distances. Norrestam & Schepper have classified the COOH and NO₂ substituents into two groups on the basis of the torsion angles. The considerable disparity in deformation parameters between the groups means that one cannot expect too close an agreement between observed and calculated values for all combinations of torsion angles of these substituents. Although the present compound contains the benzene derivatives as ionized ligands, a comparison between observed and calculated angles can still be meaningful. It should be noted that the e.s.d.'s of the angles of the ligands are about twice and those of the *o*-nitrobenzoic acid about three times the e.s.d.'s of the angles for compounds accepted by Norrestam & Schepper into their analysis.

The *o*-nitrobenzoic acid and one of the ligands belong to the same group on the basis of the torsion angles of the substituents: in each the COOH (COO⁻) substituent is coplanar and the NO₂ substituent orthogonal (Table 3). The observed endocyclic angles are the same within 0.5° for the *o*-nitrobenzoic acid and the ligand. Likewise the r.m.s. deviation between observed and calculated angles is 1.2° for both the acid and the ligand. The large value arises because the calculated values are interchanged relative to the observed values, for the angles C(14)–C(15)–C(10) and C(13)–C(14)–C(15) in the ligand as well as for the respective angles in the acid. The interchange results in r.m.s. values of 0.4 and 0.7° for the ligand and the acid, respectively. Deviation is also considerable for the angle C(11)–C(12)–C(13) and for the corresponding angle in the acid, the calculated value being about 1.0° smaller than the observed value in each case.

The best agreement for the other ligand is obtained when COO⁻ is an orthogonal but NO₂ is a coplanar substituent (Table 3). The r.m.s. deviation between observed and calculated angles is 0.5°, and calculation yields a value 1.2° too high for the angle C(17)–C(22)–C(21). The deviations for the other angles are less than 0.6°.

Weak N...O and O...O hydrogen bonds link the complex units into a one-dimensional chain in the *a* direction (Fig. 2). Hydrogen-bonding parameters are given in Table 4. The intramolecular interactions N(1)–H(10)...O(7) and N(1)–H(11)...O(3) with angle values of 98 and 100°, N...O distances of 2.777 (6) and 2.809 (5) Å and H...O distances of 2.57 and 2.54 Å, respectively, could be interpreted as N...O contacts rather than hydrogen bonds and have therefore been omitted from figures and Table 4.

References

- BHATTACHARJEE, S. K. & AMMON, H. L. (1981). *Acta Cryst.* B37, 2082–2085.
 COLAPIETRO, M. & DOMENICANO, A. (1977). *Acta Cryst.* B33, 2240–2243.
 DHANESHWAR, N. N., KULKARNI, A. G., TAVALE, S. S. & PANT, L. M. (1975). *Acta Cryst.* B31, 1978–1980.
 DHANESHWAR, N. N., TAVALE, S. S. & PANT, L. M. (1974). *Acta Cryst.* B30, 583–587.
 DICKINSON, C., STEWART, J. M. & HOLDEN, J. R. (1966). *Acta Cryst.* 21, 663–670.
 DOMENICANO, A. & MURRAY-RUST, P. (1979). *Tetrahedron Lett.* 24, 2283–2286.
 HOLDEN, J. R., DICKINSON, C. & BOCK, C. M. (1972). *J. Phys. Chem.* 76, 3597–3602.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KLINGA, M. (1976). *Finn. Chem. Lett.* pp. 179–180.
 KLINGA, M. (1979). *Finn. Chem. Lett.* pp. 223–226.
 MUHONEN, H. (1982). *Acta Cryst.* B38, 2041–2043.
 MUHONEN, H. & HÄMÄLÄINEN, R. (1978). *Acta Chem. Scand. Ser. A*, 32, 121–125.
 NORRESTAM, R. & SCHEPPER, L. (1981). *Acta Chem. Scand. Ser. A*, 35, 91–103.
 ORAMA, O. (1976). *Ann. Acad. Sci. Fenn. Ser. A2*, No. 180, p. 7.
 ORAMA, O., HUTTNER, G., LORENZ, H., MARSILI, M. & FRANK, A. (1976). *Finn. Chem. Lett.* pp. 137–139.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 TAVALE, S. S. & PANT, L. M. (1973). *Acta Cryst.* B29, 2979–2980.

Acta Cryst. (1983). C39, 540–542

Structure of Erbium Ditartrate Trihydrate, Er⁴⁺·2C₄H₄O₆²⁻·3H₂O

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Abstract. $M_r = 517.45$, tetragonal, $P4_12_12$, $a = 0.71069$ Å, $\mu = 6.74$ mm⁻¹, $F(000) = 1000$, $T = 5.995$ (1), $b = 5.995$ (1), $c = 36.433$ (8) Å, $V = 273$ K. Final $R = 0.045$ for 1704 observed reflexions. Erbium and hydrogen bonds involving water link the