stereochemistry, a comparability that is reflected in the similarity of the electronic reflectance spectra, Table 7.

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The Crystal and Molecular Structure of Aquabis[L-(+)-*threo*-2-amino-1-phenyl-1,3-propanediolato-N,O^1]copper(II) Tetrahydrate

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Abstract

The crystal structure of $Cu(C_9H_{12}NO_2)_2(H_2O).4H_2O$, $C_{18}H_{26}CuN_2O_5.4H_2O$, has been refined to $R = 0.036$ for 1747 counter reflections: $a = 12.582$ (9), $b = 26.076$ (15), $c = 6.954$ (8) Å, space group $P2_12_12$, $Z = 4$. The structure consists of aquabis[L-(+)-*threo*-2-amino-1-phenyl-1,3-propanediolato-N,O^1]copper(II) neutral complexes and water molecules linked by hydrogen bonds. The coordination polyhedron of Cu is a square pyramid whose base is formed by two N atoms [Cu—N = 1.989 (7), 1.995 (7) Å] and two O atoms from hydroxylate groups [Cu—O = 1.915 (4), 1.927 (4) Å] which are adjacent to the phenyl groups, belonging to two chelating ligands. A water molecule is at the apex of the pyramid [Cu—O_w = 2.440 (8) Å].

Introduction

Equilibria studies of L-(+)-*threo*-2-amino-1-phenyl-1,3-propanediol with protons and Cu^{II} ions in aqueous solutions (Braibanti, Mori & Dallavalle, 1978) indicate the existence of several kinds of Cu^{II} complexes. In addition to that formed by the neutral (H_2L) ligand, others are formed by the deprotonated organic ligand involving the ionization of an OH group (HL^-), probably that adjacent to the phenyl group. These complexes should contain five-membered chelate rings, with amine N and hydroxylate O as donor atoms. An analysis of the complex $Cu(HL)_2.5H_2O$ has been carried out to confirm the type of coordination in these complexes.

Experimental

Preparation

Crystals of the complex were obtained from an aqueous alkaline solution of copper chloride treated with an excess of ligand and gently heated. Blue–violet crystals separated on standing.

Crystal data

$C_{18}H_{26}CuN_2O_5.4H_2O$, $M_r = 486.0$, orthorhombic, $a = 12.582$ (9), $b = 26.076$ (15), $c = 6.954$ (8) Å, $V = 2282$ (4) Å^3, $D_c = 1.415$ Mg m^{-3}, $Z = 4$, $F(000) = 1028$, Mo $K\alpha$ radiation, $\bar{\lambda} = 0.71069$ Å, μ(Mo $K\alpha$) = 1.005 mm^{-1}, space group $P2_12_12$ from systematic absences. Cell parameters were determined from photographs and were subsequently refined from diffractometer data.

Intensity data

Intensities were collected on a Siemens AED single-crystal diffractometer with Zr-filtered Mo $K\alpha$ radiation and an ω–2θ scan. A prismatic crystal ca 0.18 × 0.33 × 0.42 mm was aligned with [001] along the φ axis of the diffractometer and all reflections with $2\theta \le 50°$ were measured. Of 2321 independent reflections, 1747 were used in the analysis [$I \ge 2\sigma(I)$]. Corrections for Lorentz and polarization factors were made, but no correction for absorption was applied. The absolute scale and overall temperature factor were obtained by Wilson's (1942) method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and refined with $SHELX$ (Sheldrick, 1976). Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for the non-hydrogen atoms. A ΔF synthesis revealed the positions of all the H atoms. Further refinement included these H atoms with isotropic thermal parameters. Unit weights were used by analyzing the variations of $|\Delta F|$ as a function of $|F_o|$. The final R was 0.036 (observed reflections only). Final atomic coordinates are given in Table 1.*

All calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.

Table 1. *Final atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z		x	y	z
Cu	1075 (1)	1950 (1)	2548 (1)	H(1)	−119 (7)	162 (3)	106 (3)
O(11)	922 (4)	2564 (1)	4083 (6)	H(2)	−131 (6)	194 (3)	290 (15)
O(12)	1348 (3)	1360 (1)	985 (6)	H(3)	347 (5)	168 (2)	−109 (10)
O(21)	−482 (7)	3237 (3)	−677 (12)	H(4)	237 (5)	156 (2)	−80 (10)
O(22)	332 (9)	501 (3)	5728 (14)	H(5)	−104 (5)	144 (2)	−141 (9)
O$_w$(1)	−817 (6)	1752 (3)	2342 (17)	H(6)	26 (6)	130 (3)	−56 (10)
O$_w$(2)	2705 (6)	1684 (3)	−1679 (11)	H(7)	−3 (6)	246 (3)	563 (10)
O$_w$(3)	−282 (7)	1287 (3)	−1553 (13)	H(8)	−126 (5)	240 (2)	589 (10)
O$_w$(4)	−539 (7)	2428 (3)	6727 (12)	H(9)	259 (8)	258 (4)	735 (15)
O$_w$(5)	2777 (9)	2558 (3)	6117 (19)	H(10)	204 (7)	258 (3)	557 (14)
N(11)	995 (8)	2422 (2)	305 (11)	H(11)	−27 (6)	294 (3)	296 (12)
N(12)	1198 (8)	1471 (2)	4773 (11)	H(12)	255 (6)	101 (3)	400 (12)
C(11)	621 (7)	2991 (3)	2990 (11)	H(13)	198 (6)	308 (3)	119 (12)
C(21)	1105 (8)	2964 (3)	978 (12)	H(14)	52 (5)	76 (3)	205 (12)
C(31)	615 (9)	3333 (3)	−462 (15)	H(15)	62 (6)	367 (3)	−6 (12)
C(41)	887 (5)	3492 (2)	4011 (9)	H(16)	91 (6)	339 (3)	−181 (12)
C(51)	67 (6)	3810 (2)	4567 (11)	H(17)	168 (6)	51 (3)	677 (12)
C(61)	304 (7)	4262 (3)	5542 (12)	H(18)	185 (6)	22 (3)	510 (12)
C(71)	1333 (8)	4391 (2)	5961 (12)	H(19)	−67 (8)	309 (4)	−159 (13)
C(81)	2153 (7)	4082 (3)	5408 (12)	H(20)	20 (10)	57 (4)	669 (14)
C(91)	1935 (6)	3630 (2)	4390 (11)	H(21)	133 (7)	237 (3)	−106 (12)
C(12)	1332 (5)	889 (2)	2029 (9)	H(22)	23 (8)	238 (3)	−14 (12)
C(22)	1703 (5)	986 (2)	4124 (10)	H(23)	35 (6)	143 (3)	494 (10)
C(32)	1448 (6)	555 (2)	5491 (10)	H(24)	157 (5)	156 (2)	589 (10)
C(42)	2020 (5)	490 (2)	1051 (10)	H(25)	−66 (6)	371 (3)	423 (12)
C(52)	3046 (5)	597 (2)	592 (10)	H(26)	−37 (6)	448 (3)	622 (12)
C(62)	3676 (5)	259 (3)	−419 (11)	H(27)	149 (6)	473 (3)	665 (11)
C(72)	3228 (6)	−206 (3)	−973 (11)	H(28)	287 (6)	418 (3)	546 (12)
C(82)	2219 (6)	−326 (2)	−502 (13)	H(29)	255 (6)	345 (3)	384 (12)
C(92)	1605 (5)	19 (2)	499 (10)	H(30)	339 (6)	91 (3)	107 (12)
				H(31)	440 (6)	35 (3)	−79 (11)
				H(32)	359 (6)	−40 (3)	−168 (11)
				H(33)	186 (6)	−67 (3)	−79 (11)
				H(34)	86 (6)	−7 (3)	80 (10)

Table 2. *Bond distances* (Å) *and angles* (°)

(a) In the coordination polyhedron

Cu–O(11)	1·927 (4)	Cu–N(12)	1·995 (7)	O(11)–Cu–N(11)	85·2 (2)	N(11)–Cu–N(12)	178·3 (4)
Cu–O(12)	1·915 (4)	Cu–O$_w$(1)	2·440 (8)	O(11)–Cu–N(12)	95·4 (2)	O$_w$(1)–Cu–O(11)	98·9 (3)
Cu–N(11)	1·989 (7)			O(12)–Cu–N(11)	93·5 (2)	O$_w$(1)–Cu–O(12)	88·4 (3)
				O(12)–Cu–N(12)	85·6 (2)	O$_w$(1)–Cu–N(11)	92·0 (4)
				O(11)–Cu–O(12)	172·6 (2)	O$_w$(1)–Cu–N(12)	89·4 (4)

(b) In the organic ligands

C(11)–O(11)	1·427 (9)	C(12)–O(12)	1·427 (6)	C(11)–H(11)	1·13 (8)	C(12)–H(14)	1·08 (6)
C(11)–C(21)	1·528 (12)	C(12)–C(22)	1·551 (9)	N(11)–H(21)	1·05 (8)	N(12)–H(23)	1·08 (8)
C(11)–C(41)	1·524 (10)	C(12)–C(42)	1·515 (8)	N(11)–H(22)	1·02 (10)	N(12)–H(24)	0·94 (7)
C(21)–N(11)	1·495 (10)	C(22)–N(12)	1·486 (9)	C(31)–H(15)	0·92 (8)	C(32)–H(17)	0·94 (8)
C(21)–C(31)	1·519 (13)	C(22)–C(32)	1·507 (9)	C(31)–H(16)	1·02 (8)	C(32)–H(18)	1·05 (8)
C(31)–O(21)	1·411 (14)	C(32)–O(22)	1·421 (14)	O(21)–H(19)	0·78 (10)	O(22)–H(20)	0·71 (10)
C(41)–C(51)	1·379 (9)	C(42)–C(52)	1·359 (9)	C(51)–H(25)	0·98 (8)	C(52)–H(30)	0·98 (8)
C(51)–C(61)	1·392 (10)	C(52)–C(62)	1·378 (10)	C(61)–H(26)	1·12 (8)	C(62)–H(31)	0·98 (8)
C(61)–C(71)	1·369 (13)	C(62)–C(72)	1·392 (11)	C(71)–H(27)	1·02 (8)	C(72)–H(32)	0·89 (8)
C(71)–C(81)	1·364 (12)	C(72)–C(82)	1·348 (11)	C(81)–H(28)	0·94 (8)	C(82)–H(33)	1·02 (8)
C(81)–C(91)	1·402 (10)	C(82)–C(92)	1·375 (9)	C(91)–H(29)	0·98 (8)	C(92)–H(34)	0·99 (8)
C(91)–C(41)	1·392 (10)	C(92)–C(42)	1·389 (8)	C(21)–H(13)	1·15 (8)	C(22)–H(12)	1·07 (8)

O(11)–C(11)–C(21)	108·8 (6)	O(12)–C(12)–C(22)	109·5 (4)	H(21)–N(11)–H(22)	95 (7)	H(23)–N(12)–H(24)	115 (5)
C(11)–C(21)–N(11)	107·1 (7)	C(12)–C(22)–N(12)	107·2 (5)	H(15)–C(31)–C(21)	114 (5)	H(17)–C(32)–C(22)	128 (5)
N(11)–C(21)–C(31)	110·8 (7)	N(12)–C(22)–C(32)	110·6 (6)	H(15)–C(31)–O(21)	102 (5)	H(17)–C(32)–O(22)	101 (5)
C(11)–C(21)–C(31)	114·4 (8)	C(12)–C(22)–C(32)	114·0 (5)	H(16)–C(31)–C(21)	123 (4)	H(18)–C(32)–C(22)	111 (4)
C(21)–C(31)–O(21)	110·8 (8)	C(22)–C(32)–O(22)	111·0 (6)	H(15)–C(31)–H(16)	98 (7)	H(17)–C(32)–H(18)	90 (7)
O(11)–C(11)–C(41)	110·4 (6)	O(12)–C(12)–C(42)	110·8 (5)	H(16)–C(31)–O(21)	107 (4)	H(18)–C(32)–O(22)	115 (4)
C(21)–C(11)–C(41)	112·3 (6)	C(22)–C(12)–C(42)	111·2 (5)	H(19)–O(21)–C(31)	118 (7)	H(20)–O(22)–C(32)	108 (5)
C(11)–C(41)–C(51)	118·8 (6)	C(12)–C(42)–C(52)	120·5 (5)	H(25)–C(51)–C(41)	118 (5)	H(30)–C(52)–C(42)	121 (5)
C(11)–C(41)–C(91)	121·2 (6)	C(12)–C(42)–C(92)	121·1 (6)	H(25)–C(51)–C(61)	123 (5)	H(30)–C(52)–C(62)	117 (5)
C(51)–C(41)–C(91)	120·0 (5)	C(52)–C(42)–C(92)	118·3 (6)	H(26)–C(61)–C(51)	118 (4)	H(31)–C(62)–C(52)	121 (5)
C(41)–C(51)–C(61)	119·0 (7)	C(42)–C(52)–C(62)	122·3 (6)	H(26)–C(61)–C(71)	120 (4)	H(31)–C(62)–C(72)	121 (5)
C(51)–C(61)–C(71)	121·0 (7)	C(52)–C(62)–C(72)	117·7 (6)	H(27)–C(71)–C(61)	120 (4)	H(32)–C(72)–C(62)	118 (5)
C(61)–C(71)–C(81)	120·7 (7)	C(62)–C(72)–C(82)	121·1 (7)	H(27)–C(71)–C(81)	120 (4)	H(32)–C(72)–C(82)	121 (5)
C(71)–C(81)–C(91)	119·4 (8)	C(72)–C(82)–C(92)	120·0 (6)	H(28)–C(81)–C(71)	124 (5)	H(33)–C(82)–C(72)	125 (4)
C(81)–C(91)–C(41)	119·9 (7)	C(82)–C(92)–C(42)	120·5 (6)	H(28)–C(81)–C(91)	116 (9)	H(33)–C(82)–C(92)	115 (4)
H(11)–C(11)–O(11)	104 (4)	H(14)–C(12)–O(12)	107 (4)	H(29)–C(91)–C(81)	116 (5)	H(34)–C(92)–C(82)	119 (4)
H(11)–C(11)–C(21)	112 (4)	H(14)–C(12)–C(22)	109 (4)	H(29)–C(91)–C(41)	123 (5)	H(34)–C(92)–C(42)	120 (4)
H(11)–C(11)–C(41)	109 (4)	H(14)–C(12)–C(42)	110 (4)	H(13)–C(21)–N(11)	112 (4)	H(12)–C(22)–N(12)	114 (4)
H(21)–N(11)–C(21)	112 (4)	H(23)–N(12)–C(22)	112 (4)	H(13)–C(21)–C(31)	108 (4)	H(12)–C(22)–C(32)	108 (4)
H(22)–N(11)–C(21)	107 (5)	H(24)–N(12)–C(22)	104 (4)	H(13)–C(21)–C(11)	105 (4)	H(12)–C(22)–C(12)	104 (4)

(c) In the water molecules

O$_w$(1)–H(1)	1·06 (5)	O$_w$(3)–H(6)	0·97 (7)	H(1)–O$_w$(1)–H(2)	104 (7)	H(7)–O$_w$(4)–H(8)	98 (5)
O$_w$(1)–H(2)	0·88 (8)	O$_w$(4)–H(7)	1·00 (7)	H(3)–O$_w$(2)–H(4)	100 (6)	H(9)–O$_w$(5)–H(10)	97 (9)
O$_w$(2)–H(3)	1·05 (6)	O$_w$(4)–H(8)	1·08 (7)	H(5)–O$_w$(3)–H(6)	124 (6)		
O$_w$(2)–H(4)	0·81 (7)	O$_w$(5)–H(9)	0·89 (10)				
O$_w$(3)–H(5)	1·04 (6)	O$_w$(5)–H(10)	1·00 (9)				

(d) Hydrogen bonds

O$_w$(4)···O(11)	2·686 (10)	O$_w$(4)–H(7)–O(11)	169 (7)	O$_w$(1)···O$_w$(5^{ii})	2·741 (13)	O$_w$(1)–H(2)–O$_w$(5^{ii})	169 (8)
H(7)···O(11)	1·70 (7)	H(7)–O$_w$(4)–O(11)	7 (4)	H(2)···O$_w$(5^{ii})	1·87 (8)	H(2)–O$_w$(1)–O$_w$(5^{ii})	7 (5)
O$_w$(5)···O(11)	2·654 (13)	O$_w$(5)–H(10)–O(11)	164 (9)	O$_w$(4)···O$_w$(5^{ii})	2·899 (15)	O$_w$(4)–H(8)–O$_w$(5^{ii})	162 (5)
H(10)···O(11)	1·68 (9)	H(10)–O$_w$(5)–O(11)	10 (5)	H(8)···O$_w$(5^{ii})	1·85 (7)	H(8)–O$_w$(4)–O$_w$(5^{ii})	11 (4)
O$_w$(2)···O(12)	2·657 (9)	O$_w$(2)–H(4)–O(12)	167 (6)	O(21)···O$_w$(4^{iii})	2·778 (1)	O(21)–H(19)–O(4^{iii})	147 (10)
H(4)···O(12)	1·86 (7)	H(4)–O$_w$(2)–O(12)	9 (4)	H(19)···O$_w$(4^{iii})	2·09 (10)	H(19)–O(21)–O$_w$(4^{iii})	24 (7)
O$_w$(3)···O(12)	2·712 (10)	O$_w$(3)–H(6)–O(12)	172 (7)	O(22)···O$_w$(3^{iv})	2·894 (12)	O(22)–H(20)–O$_w$(3^{iv})	140 (8)
H(6)···O(12)	1·75 (7)	H(6)–O$_w$(3)–O(12)	5 (4)	H(20)···O$_w$(3^{iv})	2·31 (10)	H(20)–O(22)–O$_w$(3^{iv})	31 (8)
O$_w$(2)···O(21^i)	2·816 (12)	O$_w$(2)–H(3)–O(21^i)	159 (6)				
H(3)···O(21^i)	1·82 (7)	H(3)–O$_w$(2)–O(21^i)	14 (4)				

(e) Symmetry code

(i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$ (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ (iii) $x, y, -1 + z$ (iv) $x, y, 1 + z$

Discussion of the structure

The structure (Fig. 1) consists of [Cu(HL)$_2$(H$_2$O)] neutral complexes and water molecules linked by hydrogen bonds. Bond distances and angles are given in Table 2. The Cu coordination polyhedron is a square pyramid whose base is occupied by two N atoms and two O atoms, in *trans* positions, from two ligands chelated through the amine and the ionized hydroxy groups, the latter being adjacent to the phenyl group (Fig. 2). The Cu–N and Cu–O lengths in the basal plane correspond well to values found in similar compounds. The four atoms forming the base of the pyramid have a slight tetrahedral distortion as shown

Table 3. *Least-squares planes*

Equations of least-squares planes are in the form $AX + BY + CZ = D$, where X, Y and Z are coordinates in Å. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	A	B	C	D

Plane 1: O(11), O(12), N(11), N(12)

| | −0·9909 | −0·1322 | −0·0257 | −2·1321 |

[O(11) −0·062 (5), O(12) −0·035 (4), N(11) 0·051 (10), N(12) 0·046 (10), Cu 0·074 (1), O_w(1) 2·505 (8)]

Plane 2: O(11), N(11), C(11), C(21), C(31), O(12), N(12), C(12), C(22), C(32), Cu

| | −0·9818 | −0·1704 | −0·0843 | −2·4124 |

[O(11) −0·192 (5), N(11) 0·089 (10), C(11) 0·141 (9), C(21) −0·327 (10), C(31) 0·199 (11), O(12) 0·085 (4), N(12) −0·001 (10), C(12) 0·253 (6), C(22) −0·371 (6), C(32) 0·055 (8), Cu 0·069 (1), O(21) 1·609 (9), O(22) 1·444 (11), O_w(1) 2·506 (8)]

Plane 3: C(41), C(51), C(61), C(71), C(81), C(91)

| | 0·0574 | 0·4906 | −0·8695 | 2·1154 |

[C(41) −0·009 (6), C(51) 0·002 (7), C(61) 0·008 (8), C(71) −0·006 (8), C(81) −0·008 (8), C(91) 0·014 (7)]

Plane 4: C(42), C(52), C(62), C(72), C(82), C(92)

| | −0·3087 | 0·4066 | −0·8599 | −0·9000 |

[C(42) 0·007 (7), C(52) −0·104 (1), C(62) −0·003 (8), C(72) 0·010 (8), C(82) −0·007 (8), C(92) −0·002 (7)]
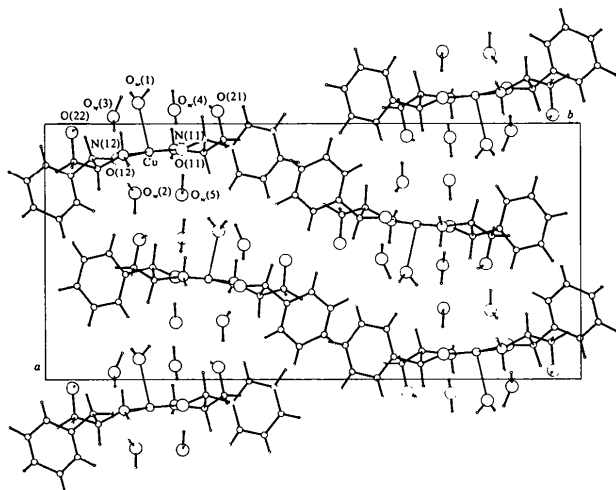

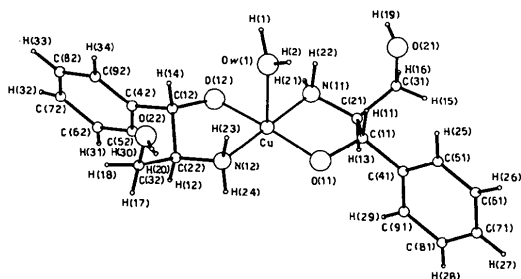Fig. 1. Projection of the structure on (001).

Fig. 2. View of the complex with the atom numbering.

by their displacements from the mean plane through them. The Cu atom is displaced by 0·07 Å towards the apex of the pyramid (Table 3) which is occupied by the water molecule O_w(1) at a distance (2·44 Å) in good agreement with those generally found for complexes of this type. The sixth octahedral site is completely free.

An analysis of the planarity (Table 3) shows that the plane through the Cu atom and the aminopropanolate moieties of both ligands [the maximum deviations are −0·327 Å for C(21) and −0·371 Å for C(22)] leaves the hydroxy O atoms and the water molecule, O_w(1), on the same side. The angles which this plane forms with the C(31)—O(21) and C(32)—O(22) bonds are 88 and 78° respectively and the angles which the same plane forms with the phenyl rings [C(41)—C(91) and C(42)—C(92)] are 86 and 72° respectively.

A comparison of the structural parameters of the ligand with those of the uncomplexed N-protonated D-(−)-*threo* stereoisomer (Wilhelm & Fischer, 1976a,b) shows that the main variations concern the angles O—C—C not involving C atoms of the phenyl rings. The increase of the angle O—C—C involving the hydroxylate O atom adjacent to the phenyl group, apparent in the chelating ligand, can be related to steric effects due to the chelation, while the decrease of the O—C—C angle involving the other O atom can be explained by the different hydrogen bonds in which the OH groups are involved.

The data collected in Table 4 show that the conformation of the pentaatomic chelate rings is a half-chair.

Packing is determined by a dense network of inter-molecular hydrogen bonds involving both types of O atoms and the surrounding water molecules.

Table 4. *Conformation of the pentaatomic chelate rings*

(a) Equations of least-squares planes (see Table 3). Displacements (Å) of relevant atoms from the planes are in square brackets.

Plane (a): Cu, N(11), O(11)

$$0·9975X + 0·0708Y − 0·0085Z = 1·6938$$

[Cu 0, N(11) 0, O(11) 0, C(11) −0·380 (9), C(21) 0·234 (10)]

Plane (b): Cu, N(12), O(12)

$$−0·9817X − 0·1838Y − 0·0501Z = −2·3510$$

[Cu 0, N(12) 0, O(12) 0, C(12) 0·209 (6), C(22) −0·369 (6)]

(b) Torsion angles (°)

Ring: Cu, N(11), C(11), C(21), O(11)

C(21)—C(11)—O(11)—Cu	38·7
C(11)—O(11)—Cu—N(11)	−16·7
O(11)—Cu—N(11)—C(21)	−9·6
Cu—N(11)—C(21)—C(11)	31·6
N(11)—C(21)—C(11)—O(11)	−45·5

Ring: Cu, N(12), C(12), C(22), O(12)

C(22)—C(12)—O(12)—Cu	30·6
C(12)—O(12)—Cu—N(12)	−9·2
O(12)—Cu—N(12)—C(22)	−15·3
Cu—N(12)—C(22)—C(12)	34·0
N(12)—C(22)—C(12)—O(12)	−41·9

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The Crystal and Molecular Structure of the 2:1 Salt Bis(*N*-methylphenazinium) Bis(maleodinitriledithiolato)nickelate(II), [(NMP)₂]²⁺[Ni(mnt)₂]²⁻

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Abstract

$[(C_{13}H_{11}N_2)_2]^{2+}[NiS_4C_4(CN)_4]^{2-}$, $M_r = 729\cdot6$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 11\cdot987$ (5), $b = 8\cdot639$ (4), $c = 16\cdot481$ (13) Å, $\beta = 106\cdot05$ (5)°, $V = 1640$ Å³, $Z = 2$, $d_{calc} = 1\cdot477$ Mg m⁻³. The structure, including H, was solved by Patterson and Fourier methods and refined by least-squares calculations to $R = 0\cdot041$, based on 1144 observations. Planar [Ni(mnt)₂]²⁻ anions are sandwiched between slightly bent (4°) [NMP]⁺ cations. The interplanar separation is 3·48 Å. The triads are stacked along a with an interplanar separation between adjacent triads of 3·35 Å and a very weak electronic overlap. The compressed pellet conductivity is 6×10^{-3} Ω^{-1} m⁻¹.

Introduction

One of the systems of interest in the field of solids with 'low-dimensional' physical properties (Keller, 1977; Miller, 1978) are charge-transfer compounds consisting of planar organic donor molecules and planar transition-metal complexes as acceptors. The best suited transition-metal complexes appear to be bis(1,2-dithiolato) complexes of the nickel triad, which readily undergo electron-transfer reactions. Reviews of the properties of such complexes have been published by McCleverty (1968) and Eisenberg (1970). Some solids consisting of those anions and of nonconducting cations exhibit moderate to high electrical conductivities, up to 100 Ω^{-1} m⁻¹ for compressed pellets (Perez-Albuerne, Isett & Haller, 1977). These high

conductivities imply the occurrence of a stacked structure of anions in the crystals. This kind of structure has been found in $[(C_2H_5)_4N][Ni(mnt)_2]$ with a room-temperature resistivity of $3\cdot5 \times 10^3$ Ω m in the stack direction (Kobayashi & Sasaki, 1977), and in $[(n-C_4H_9)_4N][Cu(mnt)_2]$ (Forrester, Zalkin & Templeton, 1964). Electrical conductivity has also been found in salts of bis(1,2-dithiolato) complexes with planar organic donors such as tetrathiafulvalene (TTF), *e.g.* $(TTF)_2[M(mnt)_2]$, $M = Cu$, Co, Ni, Pt, and (TTF)-[Pt(mnt)₂], $\sigma < 10^{-4}$ Ω^{-1} m⁻¹ (Wudl, 1975); (TTF)-[Ni(mnt)₂], $\sigma = 5 \times 10^{-2}$ Ω^{-1} m⁻¹ (Wudl, Ho & Nagel, 1973); $(TTF)_2[NiS_4C_4H_4]$, $\sigma = 0\cdot1$ Ω^{-1} m⁻¹ (Interrante, Browall, Hart, Jacobs, Watkins & Wee, 1975). With tetrathiatetracene (TTT) as a donor, observed conductivities were 30 Ω^{-1} m⁻¹ for $(TTT)_2$-[Pt(mnt)₂] and 1 Ω^{-1} m⁻¹ for (TTT)[Pt(mnt)₂] (Wheland & Gilson, 1976), and 3×10^3 Ω^{-1} m⁻¹ for $(TTT)_{1\cdot2}[NiS_4C_4H_4]$ (Interrante, Bray, Hart, Kasper, Piacente & Watkins, 1977). In (perylene)₂-[M(mnt)₂], $M = Ni$, Cu, Pd, single-crystal conductivities of 5×10^3 Ω^{-1} m⁻¹ have been detected (Alcacer & Maki, 1974), and the occurrence of stacks of perylene with a formal charge of $\frac{1}{2}$ per molecule has been suggested. As one unit-cell axis is only 4·06 Å, the metal complexes should form stacks, too. Yet in all the complete structure determinations of salts of bis(1,2-dithiolato)metal complex anions and planar organic cations, no segregated stacks of anions and cations have been found. Stacks of alternating cations and anions occur in nonconducting $(TTF)[CuS_4C_4(CF_3)_4]$ (Bray, Hart, Interrante, Jacobs, Kasper, Watkins, Wee & Bonner, 1975), and in semiconducting ($\sigma = 10^{-3}$ Ω^{-1} m⁻¹ for single crystals) 1:1 adducts of perylene and pyrene with $NiS_4C_4(CF_3)_4$ (Schmitt, Wing & Maki, 1969). Regular stacks of the donor have been