Unexpected five-coordination in di(1,3-diaminopropane)-3,5-dinitrobenzoatocopper(II) 3,5-dinitrobenzoate. Comparison between the coordinated and non-coordinated anions

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Abstract

The crystal and molecular structure of di(1,3-diaminopropane)-3,5-dinitrobenzoatocopper(II) 3,5-dinitrobenzoate $(C_{13}H_{23}CuN_6O_6)^+(C_7H_3N_2O_6)^-$ was determined by single crystal X-ray methods. The compound crystallizes in the monoclinic system, space group $P2_1/c$, $a = 19.378(9)$, $b = 6.358(2)$, $c = 22.549(9)$ Å, $\beta = 107$ 48(3)°, $Z = 4$, $D_c = 1.59$, $D_m = 1.60(1)$ g/cm³. The final R value for 2746 reflections was 0.037 ($R_w = 0.035$, $1/\sigma^2$ weights). Only one of the two 3,5-dinitrobenzoate anions is coordinated via one carboxylate oxygen with the bond length of 2.252(3) Å. Thus the coordination around the central Cu^{II} ion is 4+1 and the site symmetry approximately C_{2v}. The coordination mode 4+1 is the first reported among the series consisting of variously substituted benzoates and bis(1,3-diaminopropane)copper(II) cations. The non-coordinated 3,5-dinitrobenzoate anion is bonded by hydrogen bonds to the neighbouring amines. The $\nu_{as}(CO_2)$ vibrations for both anions appear at about 1609 cm^{-1}, whereas the $\nu_s(CO_2)$ is seen at 1335 and 1527 cm^{-1} for the coordinated and non-coordinated anions, respectively. *Ab initio* calculations with the 3-21G* basis set for 3,5-dinitrobenzoic acid and its anion reveal elongation of the bond between the carboxylate group and aromatic ring upon deprotonation of the acid. The complexation of the anion does not cause any clear difference in the bond length. The charge densities obtained by the STO-3G* basis set show that the oxygen coordinated to the copper(II) cation carries more negative charge than the non-coordinated oxygen. In the non-coordinated anion the charge densities are more evenly distributed.

Key words: Crystal structures; Copper complexes, Bidentate ligand complexes; Chelate complexes; Amine complexes

Introduction

In our systematic studies on di(1,3-diaminopropane)copper(II) cation (1,3-diaminopropane = tn) and variously substituted benzoates as a counter ion, we have obtained a series of coordination polyhedra of the 4+2 type [1, 2]. In every compound there is a benzoate anion semi-coordinated via one of the two carboxylate oxygens. The site symmetry around the central Cu(II) ion is C_i. There is only one exception reported so far: in aqua-*meta*-iodobenzoato-di(1,3-diaminopropane)copper(II) *meta*-iodobenzoate the coordination around copper is 4+1+1 [3]. Thus there are no compounds in the series displaying five-coordination. However, five-coordination is observed in $[(tn)_2Cu(tn)Cu(tn)_2]ClO_4$, $CuSO_4(tn)_2$ and $CuSeO_4(tn)_2$ [4, 5]. Related with the problem of coordination number, there is a review article of *cis*-distortion in six-coordinated copper(II) complexes, where asymmetric distortion leads from six-coordination into five-coordination [6].

In a historical note, the concept of 'semi-coordination' was introduced by Brown *et al.* to describe a long axial distance between a copper(II) ion and a weakly coordinated anion. The coordination was said to produce slight distortions in a coordinated anion, but clear enough to be detected by IR spectroscopy [7].

In this paper we report the results of single-crystal analysis of 3,5-dinitrobenzoato-di(1,3-diaminopropane)copper(II) 3,5-dinitrobenzoate, which is the first example in the series of $Cu(tn)_2$ benzoates showing five-coordination. A special emphasis is laid upon differences between the coordinated and non-coordinated anion. Because the axial bond in the copper(II) complexes with square pyramidal coordination polyhedron is clearly shorter than in elongated pseudo-octahedral polyhedra, the differences should also be more clearly

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seen *Ab initio* calculations for the 3,5-dinitrobenzoic acid, its anion and the observed structure were performed to evaluate the possible electronic differences caused by deprotonation and complexation.

Experimental

Synthesis

The title compound was synthesized by dispersing 0.02 mol of 3,5-dinitrobenzoic acid with 0.01 mol of $CuCO_3$ into a solution of 100 ml H_2O and 50 ml EtOH. The dispersion was heated and stirred until there was a homogeneous blue precipitate. After addition of 0.02 mol of tn a deep blue solution was obtained; deep blue crystals were separated after 4 h cooling.

IR spectrum and UV–Vis spectrum

These were recorded as reported in our earlier paper [1].

Crystal data

$C_{20}H_{26}CuN_8O_{12}$, $M = 634.02$, monoclinic, $a = 19.378(9)$, $b = 6.358(2)$, $c = 22.549(9)$ Å, $\beta = 107.48(3)°$, $U = 2650(2)$ Å^3 (by least-squares refinement of diffractometer angles for 16 independent well-centred reflections, $\lambda = 0.71069$ Å), space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.59$, $D_m = 1.60(1)$ g cm^{-3}, $F(000) = 1308$. Dark blue prisms. Crystal dimensions $0.35 \times 0.40 \times 0.45$ mm, $\mu = 0.898$ mm^{-1}.

Data collection and processing

Nicolet P3 diffractometer, ω scan mode, variable scan speed 2.0–30.0° min^{-1}, graphite monochromated Mo Kα radiation, 3560 unique reflections measured ($5 \leqslant 2\theta \leqslant 55°$), no absorption correction, giving 2746 independent reflections with $F > 4\sigma(F_o)$. No decay, but Lorentz and polarization corrections were made.

Structure analysis and refinement

Direct methods followed by difference Fourier techniques. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with fixed U_{iso} ($= 0.060$ Å^2). The weighting scheme $w = 1/[\sigma^2(F_o)]$ with F_o from counting statistics gave satisfactory agreement analyses. Final R and R' values are 0.037, 0.035. The neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package. The calculations were carried out with XTAL software [8].

Ab initio calculations were carried out by the Gaussian 92 program package [9]. The properties of chemical bonding were evaluated by the NBO subprogram [10]. The structure of 3,5-dinitrobenzoic acid and its anion were optimized by using STO-3G* and 3-21G* basis sets. The NBO analysis was performed separately for the complex unit and the non-coordinated anion with the STO-3G* basis set. This basis set is the only one in the Gaussian package to allow calculations with the d orbitals for copper complexes. Coordinates obtained from the single crystal structure determination were used as input. The calculations were run on CRAY X-MP, Convex C220 and VAX 8650 computers of the Computer Centre of the Finnish State.

Results and discussion

The final atomic coordinates are reported in Table 1. The bond lengths and angles for the non-hydrogen atoms for the coordination polyhedron are given in Table 2, with atoms labelled as in Fig 1. The structure consists of 3,5-dinitrobenzoato-bis(1,3-diaminopropane)-copper(II) cations and 3,5-dinitrobenzoate anions. The central Cu atom displays slightly distorted square py-

TABLE 1 Positional and isotropic thermal parameters for the atoms in the asymmetric unit with their standard deviations

	x/a	*y/b*	*z/c*	$U_{eq}{}^a$
Cu(1)	0.24444(3)	0.18679(7)	−0.12001(2)	0.0357(2)
N(1)	0.3117(2)	0.0106(5)	−0.0517(2)	0.044(1)
N(2)	0.3291(2)	0.3884(5)	−0.1092(2)	0.041(1)
N(3)	0.1869(2)	0.3422(5)	−0.1964(2)	0.045(1)
N(4)	0.1718(2)	−0.0511(5)	−0.1444(2)	0.045(1)
N(5)	0.0195(2)	0.3422(8)	0.0811(2)	0.071(2)
N(6)	0.1661(3)	0.9856(7)	0.1281(2)	0.069(2)
O(1)	0.1900(2)	0.3067(5)	−0.0515(1)	0.050(1)
O(2)	0.2414(2)	0.6197(5)	−0.0414(2)	0.068(2)
O(3)	−0.0119(2)	0.4026(7)	0.1173(2)	0.105(2)
O(4)	0.0056(2)	0.1762(7)	0.0529(2)	0.085(2)
O(5)	0.2158(3)	1.0873(6)	0.1201(2)	0.095(2)
O(6)	0.1308(3)	1.0312(7)	0.1627(2)	0.109(2)
C(1)	0.3809(2)	−0.0490(7)	−0.0619(2)	0.051(2)
C(2)	0.4279(2)	0.1393(7)	−0.0612(2)	0.052(2)
C(3)	0.3978(2)	0.2957(8)	−0.1121(2)	0.055(2)
C(4)	0.1091(2)	0.3664(7)	−0.2049(2)	0.053(2)
C(5)	0.0722(3)	0.1589(9)	−0.2135(3)	0.081(3)
C(6)	0.0943(3)	0.0074(9)	−0.1622(3)	0.076(2)
C(7)	0.1621(2)	0.5450(6)	0.0171(2)	0.038(2)
C(8)	0.1107(2)	0.4139(7)	0.0281(2)	0.043(2)
C(9)	0.0760(2)	0.4776(7)	0.0712(2)	0.049(2)
C(10)	0.0929(3)	0.6619(8)	0.1040(2)	0.056(2)
C(11)	0.1448(3)	0.7852(7)	0.0923(2)	0.052(2)
C(12)	0.1790(2)	0.7353(6)	0.0495(2)	0.045(2)
C(13)	0.2014(2)	0.4864(7)	−0.0293(2)	0.041(2)
O(1n)	0.2337(3)	−0.0069(7)	−0.2604(2)	0.155(3)
O(2n)	0.2735(2)	−0.2818(5)	−0.2037(1)	0.059(1)
O(3n)	0.4077(2)	−0.0246(6)	−0.4528(2)	0.084(2)
O(4n)	0.3381(2)	0.1944(6)	−0.4246(2)	0.070(1)
O(5n)	0.4464(2)	−0.7376(5)	−0.2609(2)	0.080(2)
O(6n)	0.4885(2)	−0.6526(6)	−0.3356(2)	0.090(2)

(*continued*)

TABLE 1 (*continued*)

	x/a	y/b	z/c	$U_{eq}{}^a$
N(5n)	0.3710(2)	0.0289(7)	−0.4192(2)	0.058(2)
N(6n)	0.4502(2)	−0.6199(6)	−0.3024(2)	0.060(2)
C(7n)	0.3210(2)	−0.2058(7)	−0.2865(2)	0.038(2)
C(8n)	0.3237(2)	−0.0686(6)	−0.3334(2)	0.041(2)
C(9n)	0.3672(2)	−0.1189(7)	−0.3695(2)	0.042(2)
C(10n)	0.4087(2)	−0.2962(8)	−0.3613(2)	0.049(2)
C(11n)	0.4052(2)	−0.4283(7)	−0.3139(2)	0.043(2)
C(12n)	0.3625(2)	−0.3877(6)	−0.2764(2)	0.042(2)
C(13n)	0.2724(3)	−0.1590(7)	−0.2464(2)	0.054(2)
H(1)	0.2856	−0.1212	−0.0472	0.060
H(2)	0.3230	0.0931	−0.0120	0.060
H(3)	0.3141	0.4979	−0.1423	0.060
H(4)	0.3387	0.4567	−0.0673	0.060
H(5)	0.4074	−0.1478	−0.0282	0.060
H(6)	0.3706	−0.1205	−0.1031	0.060
H(7)	0.4753	0.0876	−0.0650	0.060
H(8)	0.4362	0.2125	−0.0206	0.060
H(9)	0.4339	0.4115	−0.1086	0.060
H(10)	0.3889	0.2241	−0.1533	0.060
H(11)	0.2079	0.4859	−0.1949	0.060
H(12)	0.1924	0.2647	−0.2334	0.060
H(13)	0.1815	−0.1505	−0.1086	0.060
H(14)	0.1802	−0.1251	−0.1810	0.060
H(15)	0.0870	0.4538	−0.2428	0.060
H(16)	0.1019	0.4363	−0.1677	0.060
H(17)	0.0193	0.1856	−0.2217	0.060
H(18)	0.0806	0.0908	−0.2507	0.060
H(19)	0.0647	−0.1230	−0.1745	0.060
H(20)	0.0844	0.0711	−0.1249	0.060
H(21)	0.0982	0.2762	0.0057	0.060
H(22)	0.0681	0.7047	0.1352	0.060
H(23)	0.2155	0.8317	0.0411	0.060
H(24)	0.2947	0.0644	−0.3408	0.060
H(25)	0.4398	−0.3294	−0.3885	0.060
H(26)	0.3605	−0.4871	−0.2428	0.060

${}^aU_{eq}$ has been defined as $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}(a_i^*a_j^*)(\mathbf{a}_i\cdot\mathbf{a}_j)$.

ramidal five-coordination. Four basal sites are occupied by the nitrogen atoms of the tn molecules. Only one of the two benzoate anions necessary for the electroneutrality is unidentately coordinated in the apical position. The bond length Cu–O(1) is 2.252(3) Å, which is clearly shorter than the values reported for $CuSO_4(tn)_2$, 2.57(1) and $CuSeO_4(tn)_2$, 2.52(1) Å [5]. However, in the two CuN_5 chromophores of $[(tn)_2Cu(tn)Cu(tn)_2]ClO_4$ the apical Cu–N distances are 2.25(1) and 2.26(1) Å [4]. The distance between the nearest oxygen of the other carboxylate group and the Cu ion is 3.281(3) Å, which is too long a distance to indicate any interaction. Also the intermolecular Cu–O(2) distance of 3.285(3) Å is too long to be described as a bond. Furthermore, no other intermolecular distances to Cu atoms are less than this value. In $CuSO_4(tn)_2$ and $CuSeO_4(tn)_2$ the central Cu(II) ion lies strictly on the CuN_4 plane, whereas in our compound the Cu atom is displaced from the mean plane through the four basal nitrogens by 0.205(1) Å towards the apical O atom. As stated by Morosin and Howatson, the displacement of the copper(II) atom from the N_4 plane depends on the Cu–O distance [5]. It is interesting that in $[(tn)_2Cu(tn)Cu(tn)_2]ClO_4$ the displacements for the two copper(II) ions are 0.323(3) and 0.315(3) Å, respectively [4]. Although the apical distances are very similar in $[(tn)_2Cu(tn)Cu(tn)_2]ClO_4$ and in our compound, the displacements clearly differ.

TABLE 2. Bond distances (Å) and angles (°) with their standard deviations for the non-hydrogen atoms in the coordination polyhedron and chelate rings

Cu(1)–N(1)	2.031(3)	N(1)–Cu(1)–N(2)	86.9(1)
Cu(1)–N(2)	2.038(3)	N(1)–Cu(1)–N(3)	170.8(2)
Cu(1)–N(3)	2.008(3)	N(1)–Cu(1)–N(4)	91.7(1)
Cu(1)–N(4)	2.027(3)	N(1)–Cu(1)–O(1)	89.6(1)
Cu(1)–O(1)	2.250(3)	N(2)–Cu(1)–N(3)	90.7(1)
N(1)–C(1)	1.477(6)	N(2)–Cu(1)–N(4)	166.0(1)
N(2)–C(3)	1.477(6)	N(2)–Cu(1)–O(1)	103.4(1)
N(3)–C(4)	1.470(6)	N(3)–Cu(1)–N(4)	88.4(1)
N(4)–C(6)	1.481(6)	N(3)–Cu(1)–O(1)	99.7(1)
C(1)–C(2)	1.501(6)	N(4)–Cu(1)–O(1)	90.5(1)
C(2)–C(3)	1.500(6)	Cu(1)–N(1)–C(1)	115.4(3)
C(4)–C(5)	1.484(7)	Cu(1)–N(2)–C(3)	116.6(3)
C(5)–C(6)	1.466(8)	Cu(1)–N(3)–C(4)	116.5(3)
		Cu(1)–N(4)–C(6)	116.8(3)
		Cu(1)–O(1)–C(13)	121.6(3)
		N(1)–C(1)–C(2)	111.7(4)
		C(1)–C(2)–C(3)	115.2(3)
		N(2)–C(3)–C(2)	112.2(4)
		N(3)–C(4)–C(5)	111.0(4)
		C(4)–C(5)–C(6)	117.8(4)
		N(4)–C(6)–C(5)	114.2(5)

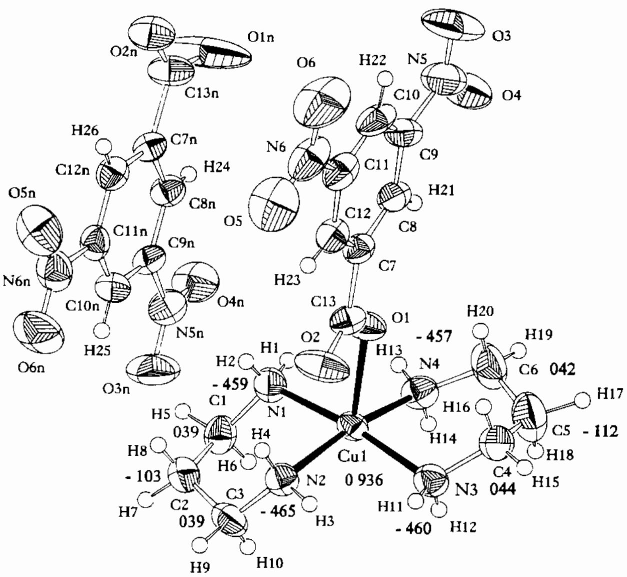

Fig. 1 The asymmetric unit of the title compound with the numbering scheme The thermal ellipsoids are scaled to 50% probability level. The charge densities at the non-hydrogen atoms for the chelate rings are also given.

The basal coordination plane consisting of the four nitrogens shows additional tetrahedral distortion, with atomic deviations from the best-fit plane in the range of +0.043(4) to −0.047(5) Å. Also the apical oxygen site shows distortion, because the N–Cu–O angles deviate markedly from 90°.

The structural pathways for the distortion of the analogous CuN_4Cl chromophore have been studied by Harrison *et al.* [11]. They consider their three distortion pathways as being related by a linear combination of the normal modes of vibration of a CuN_4Cl chromophore of C_{2v} symmetry. This symmetry corresponds to an intermediate geometry between tetragonal pyramid (C_{4v}) and trigonal bipyramid (D_{3h}). This is usually connected to the Berry rotation. The calculations based upon the Muetterties method [12] show that in our compound the coordination polyhedron is deformed only 2% from C_{4v} to D_{3h}.

The charge densities obtained by *ab initio* calculations for the chelate rings are shown in Fig. 1. The sign of the electron density located on the rings is found to obey strictly an alternating relationship such as would be required by a spin-polarization mechanism of delocalization. This finding is in good accord for the conclusions based upon NMR studies for Ni(II) complexes [13].

The UV–Vis spectrum of the compound displays a very broad, almost featureless band with a maximum at 575 nm (17.4 kK) and a shoulder at about 800 nm (12.5 kK). The small calculated deformation value for the coordination polyhedron is also in accord with the wavelength maxima reported for a regular square pyramid rather than for a distorted one [14]. On the other hand, the maxima found here are also very near to the values for *trans*-dibenzoato-bis(1,3-diaminopropane)copper(II) (17.2 and 11.6 kK) which has a centrosymmetric CuN_4O_2 coordination polyhedron. In *trans*-di-4-chlorobenzoato-bis(1,3-diaminopropane)copper(II) the maximum is seen at 17.2 kK and a shoulder at 11.7 kK [15].

In their study on d–s mixing as a rationale for structural similarities between hexacoordinated Ni(II) and Cu(II) complexes Ceulemans and Vanquickenborne suggest that 4+1 (or 4+1+1) coordination should be more common than 4+2 [16]. In a series of fourteen *trans*-di(benzoato)-bis(1,3-diaminopropane)copper(II) complexes (where benzoato can be either unsubstituted or substituted), all the copper(II) ions display 4+2 coordination. However, in aqua-*meta*-iodobenzoato-di(1,3-diaminopropane)copper(II) *meta*-iodobenzoate the coordination around copper is 4+1+1 [3]. In waterless solution it is also possible to synthesize the 'normal' *trans*-di(*meta*-iodobenzoato)-bis(1,3-diaminopropane)copper(II) complex [2]. According to Brown, the coordination number depends on the Lewis base strength [17]. The five-coordination is supposed to require a strong Lewis base. However, the present series of *trans*-di(benzoato)-bis(1,3-diaminopropane)copper(II) complexes seems to follow the reverse order, because benzoate anions are stronger Lewis bases than a sulfate or selenate anion. As stated before, there is five-coordination in $CuSO_4$(tn) and $CuSeO_4$(tn). The acids used so far have rather similar pK_a values in the range 3.41–4.27. For 2-nitrobenzoate the pK_a value is 2.16 [18]; there is six-coordination in the respective Cu(tn)$_2$ complex. However, the benzoate anion is not coordinated but the axial positions are occupied by water molecules [19]. The pK_a value for 3,5-dinitrobenzoic acid is 2.68 [20]. Thus there may be two competing pathways, one leading to five-coordination and the other leading to hydrated complexes, when the Lewis base strength diminishes.

The IR spectrum shows the following bands in the range 1800–1300 cm^{-1}: 1609(s,b), 1574(m), 1527(s), 1449(m) and 1335(vs). The bands at 1574 and 1449 cm^{-1} are very near to the values 1580 and 1450 cm^{-1} assigned to HNH scissoring and HCH scissoring vibrations, respectively, for [Cu(tn)$_2$](PF$_6$)$_2$ [21].

The remaining bands are obviously due to CO_2 vibrations. It is well known that the difference between the wave numbers due to antisymmetric ν_{as}(CO) and symmetric ν_s(CO) stretching vibrations is different, when a carboxylate ion is either coordinated or non-coordinated. In *trans*-di(*meta*-iodobenzoato)-bis(1,3-diaminopropane)copper(II) there are bands at 1584, 1545, 1465 and 1366 cm^{-1}. In this compound the two *meta*-iodobenzoate anions are coordinated unidentately to the central Cu^{II} ion. Obviously, the second and the third are connected with the chelate ring vibrations, and the first and fourth with CO_2 vibrations. Accordingly, we can tentatively assign the broad band at 1609 cm^{-1} to ν_{as}(CO) for both the coordinated and non-coordinated anions. The band at 1527 cm^{-1} is assigned to ν_s(CO) for the non-coordinated 3,5-dinitrobenzoate anion. Thus the band at 1335 cm^{-1} remains for the ν_s(CO) of the coordinated anion. According to Mehrotra and Bohra, the anti-symmetric CO stretching frequency increases and CO symmetric stretching frequency decreases as the M–O bond becomes stronger [22]. This is indeed the case, because the Cu–O1 bond length in the title compound is 2.252(3) Å and in *trans*-di(*meta*-iodobenzoato)-bis(1,3-diaminopropane)copper(II) it is 2.500(3) Å.

The N–H stretching vibrations are seen as a very narrow band at 3298(s) cm^{-1} and broad bands at 3280(s), 3180(s), 3104(m) and 3090(m) cm^{-1}. Thus there is a clear shift to smaller wave numbers, because in gas phase or in dilute solutions the vibrations appear at 3500–3300 cm^{-1}. There are three available explanations for this: either complex formation or hydrogen bonding;

TABLE 3. Distances (Å) and angles (°) for the suggested hydrogen bonds The atoms marked with a superscript have been generated with the indicated symmetry operator

	O ··H	O · N	O · H–N	Symmetry operator
O(2) H(2)^{i}–N(1)^{i}	1.88	2.877(5)	176	i = x, $1+y$, z
O(2) · H(13)^{i}–N(4)^{i}	2.17	3.117(4)	157	i
O(2n) ·H(12)–N(4)	2.26	3.068(5)	137	
O(2n) H(3)^{ii}–N(2)^{ii}	1.96	2.953(4)	173	ii = x, $1-y$, z
O(2n) · ·H(11)^{ii}–N(3)^{ii}	2.00	2.955(5)	160	ii
O(1n) ·H(12)–N(3)	2.07	2.936(5)	143	

TABLE 4 The atomic charges obtained from natural population analysis (NBO). All the calculations were carried out using the STO-3G* basis set. The atomic symbols refer either to coordinated or non-coordinated moiety

Atom	Acid opt	Ion opt	Ion coord	Ion non-coord
O(1)	−0.326	−0.513	−0.566	−0.523
O(2)	−0.284	−0.513	−0.444	−0.537
C(13)	0.391	0.358	0.381	0.311
C(7)	−0.005	−0.046	−0.016	0.018
C(8)	0.074	0.063	−0.039	−0.053
C(9)	−0.023	−0.071	0.091	0.082
C(10)	0.074	0.063	−0.054	−0.088
C(11)	−0.005	−0.046	0.091	0.080
C(12)	−0.044	−0.031	−0.032	−0.050
N(5)	0.248	0.247	0.293	0.293
O(3)	−0.216	−0.233	−0.229	−0.271
O(4)	−0.215	−0.253	−0.254	−0.248
N(6)	0.248	0.247	0.301	0.298
O(5)	−0.215	−0.233	−0.241	−0.252
O(6)	−0.215	−0.253	−0.233	−0.271

or both. However, complex formation alone cannot explain the broadening of a band. There are two N–H bonds with no close contacts to oxygen atoms in the crystal structure as discussed in the following chapter. Accordingly, the narrow band of the highest wave number at 3298 cm^{-1} can be assigned at least one of these bonds. Thus, hydrogen bonding would shift the bands further. In *trans*-di(*meta*-iodobenzoato)-bis(1,3-diaminopropane)copper(II) there are only four bands at 3293, 3233, 3140 and 3107 cm^{-1} [2]. The structure of this compound is similar to the title compound with regard to the hydrogen bonding system. So, there is a narrow band at the highest wave number and no suitable short distance to indicate hydrogen bonding for one of the N–H bonds. The higher number of the bands in the title compound can be explained by the lower symmetry. In *trans*-di(*meta*-iodobenzoato)-bis(1,3-diaminopropane)copper(II) the Cu^{II} ion lies at a centre of symmetry and thus there are four N–H bonds, whereas in the title compound there is no symmetry and the number of N–H bonds in the asymmetric units is eight.

The following values were applied in the search for the possible hydrogen bonds: H···O (1.96(12), N···O 2.85(9) Å; N–H···O 162(11)° [23]. The threshold values were $\pm 3\sigma$. A list of the possible hydrogen bonds is given in Table 3. The only hydrogen atoms capable of hydrogen bonding are those connected to the nitrogen atoms of the amine. The order of the bond lengths Cu–N seems to follow the order of the hydrogen bond strength. Both of the hydrogens in N(3) are hydrogen bonded; the Cu–N(3) bond is the shortest. In N(4), the values seem to indicate the weakest hydrogen bonds; however, again both hydrogens are H-bonded. Both N(1) and N(2) are singly hydrogen bonded. The corresponding Cu–N bonds are the longest. Moreover, the hydrogen bond to N(1) seems to be stronger; accordingly the Cu–N(1) bond is shorter than the Cu–N(2) bond. The standard deviations for the bonding parameters do not allow us to make decisive conclusions, yet. Obviously, more compounds must be investigated to apply statistical methods.

Although the oxygen atoms of the nitro groups carry clear negative charge, as seen from the electron population analysis (Table 4) there are no short contacts to be assigned as hydrogen bonds. Moreover, there are no short distances between the anions to indicate any interactions, as found earlier in the series of *trans*-bis(tn)copper(II) complexes where the counter ion is a substituted or unsubstituted benzoate anion. On the other hand, the charges on the oxygen atoms are clearly smaller than those on the carboxylate oxygens.

The bond length between the carboxylic and aromatic carbon atom is seemingly sensitive to bonding of the oxygen atoms of the carboxylate group. The elongation of this bond (compared with the value found in a corresponding acid) was noticed already in our earlier papers [1, 2]. In the benzoic and 3-iodobenzoic acid the distance is 1.484(6) and 1.480(6) Å, respectively, whereas in the corresponding anions of these copper(II) complexes the distances are 1.502(6) and 1.526(5) Å, respectively. *Ab initio* calculations were performed for the 3,5-dinitrobenzoic acid, its anion and the anions observed in the crystal structure to find out if the coordination has any noticeable effects on the geometry

TABLE 5. Selected bond lengths (Å) for 3,5-dinitrobenzoic acid and its anion

Bond	Acid opt	Kanters rt	Kanters lnt	Prince 1	Prince 2	Ion opt	Ion coord	Ion nonc
C(7)–C(13)	1.476	1.495(3)	1.490(2)	1.488(1)	1.492(1)	1.548	1.514(7)	1.519(7)
C(13)–O(1)	1.348	1.276(2)	1.305(2)	1.275(1)	1.280(1)	1.244	1.240(5)	1.206(7)
C(13)–O(2)	1.203	1.249(3)	1.232(2)	1.251(2)	1.243(1)	1.244	1.232(6)	1.234(6)
C(9)–N(5)	1.447	1.472(3)	1.474(2)	1.474(2)	1.476(1)	1.443	1.463(6)	1.482(6)
N(5)–O(3)	1.242	1.216(3)	1.225(1)	1.218(1)	1.216(2)	1.242	1.218(7)	1.232(6)
N(5)–O(4)	1.242	1.219(3)	1.226(1)	1.220(1)	1.210(2)	1.251	1.220(7)	1.218(6)
N(6)–O(5)	1.242	1.211(3)	1.224(1)	1.216(2)	1.225(1)	1.242	1.218(7)	1.217(6)
N(6)–O(6)	1.242	1.214(3)	1.222(2)	1.204(2)	1.209(1)	1.251	1.216(8)	1.220(7)
C(11)–N(6)	1.446	1.472(3)	1.474(2)	1.473(1)	1.464(2)	1.443	1.498(6)	1.476(6)

Acid opt: acid optimized by *ab initio* methods (3-21G*), Kanters rt: acid determined by Kanters *et al.* [24] at room temperature; Kanters lnt: acid at liquid nitrogen temperature [24], Prince 1 and 2: acid determined by Prince *et al.* [25], there are two independent molecules in the unit cell, ion opt: ion optimized by *ab initio* methods (3-21G*), ion coord: the coordinated anion, ion nonc: the non-coordinated anion

TABLE 6. Selected bond angles (°) for 3,5-dinitrobenzoic acid and its anion. The *ab initio* calculations were performed with the 3-21G* basis set. The atomic symbols refer either to coordinated or non-coordinated moiety

Angle	Acid opt	Kanters rt	Kanters lnt	Prince 1	Prince 2	Ion opt	Ion coord	Ion non-coord
C(8)–C(7)–C(13)	121.6	119.8(2)	120.3(1)	119.7(1)	119.7(1)	119.9	121.1(4)	120.3(4)
C(12)–C(7)–C(13)	117.7	119.4(2)	119.1(1)	119.6(1)	119.3(1)	119.9	119.0(4)	119.8(4)
C(7)–C(13)–O(1)	111.9	116.4(2)	114.1(1)	116.5(1)	115.7(1)	114.0	116.0(4)	116.7(5)
C(7)–C(13)–O(2)	124.6	118.4(2)	120.6(1)	118.5(1)	119.4(1)	114.0	117.6(4)	118.1(4)
O(1)–C(13)–O(2)	123.5	125.3(2)	125.0(1)	125.0(1)	124.9(1)	132.1	126.4(5)	125.1(6)
C(12)–C(11)–N(6)	118.8	118.3(2)	118.6(1)	118.5(1)	119.2(1)	120.1	117.8(5)	118.7(4)
C(10)–C(11)–N(6)	118.4	118.3(2)	118.2(1)	118.3(1)	118.3(1)	118.2	119.0(5)	118.5(4)
C(11)–N(6)–O(5)	117.1	119.0(2)	118.4(1)	118.7(1)	117.9(1)	117.8	118.2(5)	118.3(4)
C(11)–N(6)–O(6)	117.1	117.3(2)	117.4(1)	117.5(1)	117.9(1)	117.9	115.6(5)	118.0(4)
O(5)–N(6)–O(6)	125.8	123.7(2)	124.3(1)	123.8(1)	124.2(1)	124.3	126.2(5)	123.7(4)
C(8)–C(9)–N(5)	118.8	118.2(2)	117.9(1)	118.0(1)	117.5(1)	118.2	118.3(4)	118.7(4)
C(10)–C(9)–N(5)	118.8	118.7(2)	118.7(1)	118.6(1)	118.9(1)	118.2	119.3(5)	117.7(4)
C(9)–N(5)–O(3)	117.1	117.9(2)	117.5(1)	117.8(1)	117.4(1)	117.8	117.7(4)	117.4(4)
C(9)–N(5)–O(4)	117.2	117.6(2)	117.7(1)	117.9(1)	118.0(1)	117.9	119.1(5)	118.6(4)
O(3)–N(5)–O(4)	125.8	124.5(2)	124.8(1)	124.3(1)	124.6(1)	124.3	123.2(5)	124.0(4)

Kanters rt = measurement at room temperature [24], Kanters lnt = measurement at liquid nitrogen temperature [24], Prince 1 = molecule 1 [25]; Prince 2 = molecule 2 [25]

of the anion. The structural parameters are given in Tables 5 and 6.

In the optimized structure of the acid, the C(7)–C(13) bond length of 1.476 Å is indeed shorter than in the anions. It is comparable to corresponding bond lengths of 1.488(3) Å in 2,5-dinitrobenzoic acid [26] and 1.488(1)–1.495(3) Å in 3,5-dinitrobenzoic acid [24, 25] (Table 5). Surprisingly, in 2,4-dinitrobenzoic acid the bond length is longer, 1.503(4) Å [27]. The angle C(7)–C(13)–O(1) in the acid is quite small, only 111.9° (Table 6). However, it is comparable with the value of 112.8° for benzoic acid (STO-3G) [28]. On the other hand, the angle is considerably wider in the structures obtained by X-ray single crystal determinations, 117.0(2)° for 2,5-dinitrobenzoic acid and the values given in Table 6 for 3,5-dinitrobenzoic acid. Again, the value for 2,4-dinitrobenzoic acid is different, 114.3(2)° Obviously, the geometrical parameters for a carboxylate group are sensitive to electronic effects. It should be borne in mind that the acids form dimers in the solid state, whereas *ab initio* calculations assume a gas phase with no intermolecular interactions

As can be seen from Table 4, all the species show clearly uneven electron distribution. The major change occurs upon deprotonation. Expectedly, the electrons are more evenly distributed in the carboxylate group of the ion. The complexation of the carboxylate group has a clear effect on the charge densities at the oxygen atoms. The oxygen atom coordinated to copper has gained electron density, while the opposite happens with the other oxygen. Obviously the positive charge of the central Cu(II) ion has an electron attracting effect. While the C–O bonds in the optimized anion are essentially single bonds, the bond orders are different in the title compound. For the non-coordinated anion there are 3.974 and 1.992 electrons in the C13n–O1n and C13–O2n bonds, respectively. The corresponding values for the coordinated anion are 1.990 and 3.974 electrons. Although the e.s.d.s for the bond lengths are relatively big, the bond length C13n–O1n is clearly in the expected range for a double bond.

The electron density at the carboxylate carbon C(13) shows a relatively large variation. The strongest positive charge is in the optimized acid. Although the carboxylate oxygens carry clear negative charges, the carbon C(13) does not become more positive upon deprotonation. Instead, complexation seems to polarize the carboxylate group. Interestingly, the C(13)–C(7) bond lengths do not show any clear difference in the two anions.

The charge densities at the oxygen atoms in the nitro groups are evenly distributed for the acid, while in the ions a difference can be seen with simultaneous increase of negative charge. The nitrogen atoms in the observed structure seem to carry additional positive charge compared with the theoretical values. At the same time, the carbon atoms connected to the nitro groups have positive charges in the observed structure instead of negative as found for the theoretical structures.

Supplementary material

Listing of the thermal parameters, least-squares plane for the coordination plane, full listing of bond lengths and angles, and structure factor tables are available from the authors on request.

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