# Conformational flexibility of 1,3-diaminopropane in chelate rings. Redetermination of the structure of *trans*-dinitratobis(1,3-diaminopropane)copper(II)

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## Abstract

The flexibility of tn (tn = 1,3-diaminopropane) in pseudo-octahedral $MO_2tn_2$ complexes (where M = Co, Ni, Cu; O is in axial position and tn displays chair conformation) manifests itself mainly as variation in the bite angle (N–M–N), bite size (interring N–N distance) and puckering values of the chelate ring. Because the structure of *trans*-dinitratobis(1,3-diaminopropane)copper(II) determined earlier by X-ray methods had unusual values for the flexibility and a rather modest *R* value, it was used as a model compound in CFF calculations and redetermined by X-ray methods. The refinement improved from the earlier *R* index of 0.122 to 0.039. The current parameters are: $C_6H_{20}CuN_6O_6$, $M = 337.81$, orthorhombic, $a = 8.1888(9)$, $b = 10.234(2)$, $c = 16.349(2)$ Å, $V = 1370.2(3)$ Å$^3$, space group *Pcab* (No. 61), $Z = 4$. The site symmetry around the central Cu(II) ion is near to $D_{4h}$. An important deviation from the exact $D_{4h}$ symmetry is the widening of 3.2(2)° in the bite angle from the ideal 90°. The puckering values describing the distance of the three carbon atoms of tn from the $CuN_4$ plane are 0.513(11), −0.263(12) and 0.429(11) Å, which are exceptionally low values indicating a flattened ring. The optimized structure came more up to the expected statistical average bite angle value. To explain the difference between the optimized and the observed value of the bite angle, extended Huckel calculations were carried out. Both hydrogen bonding and mutual interaction of the ligands were investigated based upon the structures found from the Cambridge Structural Database. The most probable explanation for the variation in the bite angle is hydrogen bonding.

*Key words:* Crystal structures; Copper complexes; Bidentate ligand complexes; Amino complexes; Chelate complexes

## Introduction

The unit cell, reflectance spectrum and magnetic moment of *trans*-dinitratobis(1,3-diaminopropane)-copper(II) were determined by Nasanen *et al.* [1]. Later on, the crystal structure was determined by Pajunen [2]. The *R* value for the determination was rather modest, 0.122. The structure had an interesting feature: the wide bite angle N–Cu–N of 94.9(5)°.

In a CFF study on the chelate rings formed by tn, the bite angle was found to be in the range 90.0–95.0° for chair conformations [3]. The central metal ion in the calculations was Co(III) cation and the Co–N distances were fixed. Later on, the Co–N bond length was also optimized [4]. Now the bite angle for a mono chelate displaying chair conformation was 91.1°. However, the observed bite angle for *trans*-dibenzoatobis(1,3-diaminopropane)copper(II) is 87.09(14)° and for *trans*-di(3-iodobenzoato)bis(1,3-diaminopropane)copper(II) 87.1(1)° [5, 6].

The aim of the present study is to investigate the various possibilities for the deformations in the chelate ring. There are several factors which could influence the conformational properties. These are hydrogen bonding, plasticity of the coordination sphere and electronic effects.

Because of the rather modest *R* value in the earlier determination of *trans*-dinitratobis(1,3-diaminopropane)copper(II), the structure of the title compound was redetermined by single crystal X-ray diffraction methods. The molecular structure was also optimized by CFF methods. These structures were then compared with the structures found from the Cambridge Structural Database.

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## Experimental

Deep blue crystals of *trans*-dibenzoatobis(1,3-diaminopropane)copper(II) were obtained by heating and stirring a mixture of an aqueous solution containing $CuNO_3$ (Merck p.a.) and tn (Merck, for synthesis) in molar ratio 1:2.

### *Crystal data*

$C_6H_{20}CuN_6O_6$, $M = 337.81$, orthorhombic, $a = 8.1888(9)$, $b = 10.234(2)$, $c = 16.349(2)$ Å, $V = 1370.2(3)$ Å$^3$ (by least-squares refinement of diffractometer angles for 21 independent well-centered reflections, $\lambda = 0.71069$ Å), space group *Pcab* (No. 61), $Z = 4$, $D_c = 1.63$, $D_m = 1.62$ g cm$^{-3}$, $F(000) = 700$. Deep blue plates. Crystal dimensions $0.19 \times 0.23 \times 0.31$ mm, $\mu = 1.69$ mm$^{-1}$.

### *Data collection and processing*

Nicolet P3 diffractometer, $\omega$ scan mode, variable scan speed 2.0–30.0° min$^{-1}$, graphite monochromated Mo K$\alpha$ radiation, unique reflections measured $5.0 \leqslant 2\theta \leqslant 55.0°$, no absorption correction, giving 780 independent reflections with $F > 4\sigma(F_o)$. No decay, but Lorentz and polarization corrections were made.

### *Structure analysis and refinement*

The original coordinates were used as starting parameters after suitable transformation. Full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms was carried out. The isotropic overall thermal parameter was applied for the hydrogen atoms. The weighting scheme $w = 1/\sigma^2(F_o)$ (with $\sigma^2(F_o)$ from counting statistics) gave satisfactory agreement analyses. Final $R$ and $R'$ values are 0.039 and 0.033, respectively. 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 installed on a local PC [7].

### *CFF optimization and extended Hückel calculations*

These were carried out by PCMODEL [8] and CACAO [9], respectively, installed on a local PC.

## Results and discussion

The numbering of the complex unit is shown in Fig. 1. The atomic coordinates and thermal parameters are given in Table 1; the bond lengths and angles are presented in Table 2. The structure of the compound displays discrete complex units with two chelating tn molecules in chair conformation and two nitrate anions occupying axial positions. The site symmetry of the central copper(II) ion is near to $D_{4h}$, although the strict symmetry of the complex unit is $C_i$. The units are connected by a hydrogen bonding network.

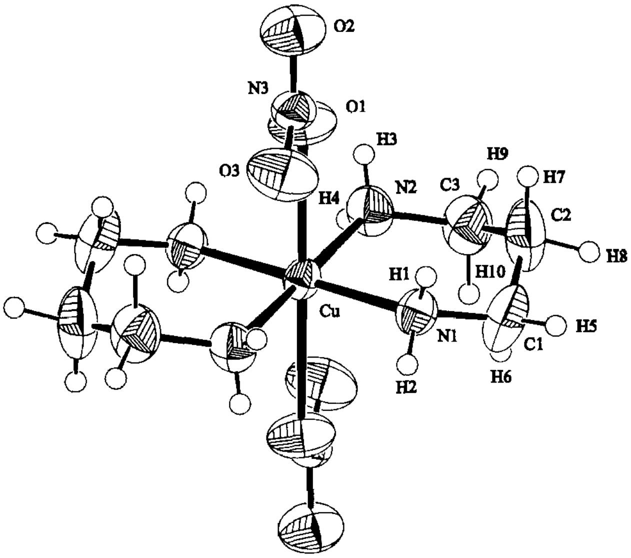

Fig. 1. ORTEP drawing of the complex unit with the numbering of the atoms. The thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

TABLE 1. Atomic positional and equivalent isotropic thermal parameters with their standard deviations

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Cu | 0 | 1/2 | 1/2 | 0.0340(2) |
| C1 | 0.116(1) | 0.6722(4) | 0.4362(8) | 0.071(3) |
| C2 | 0.129(1) | 0.6887(4) | 0.5800(8) | 0.079(3) |
| C3 | −0.009(1) | 0.6595(3) | 0.6617(6) | 0.065(2) |
| N1 | 0.1297(6) | 0.5857(2) | 0.4046(4) | 0.043(1) |
| N2 | −0.0263(6) | 0.5705(3) | 0.6615(4) | 0.052(2) |
| N3 | −0.3836(6) | 0.5768(3) | 0.4432(5) | 0.043(1) |
| O1 | −0.2631(5) | 0.5465(2) | 0.3879(4) | 0.066(1) |
| O2 | −0.4989(5) | 0.5985(2) | 0.3741(4) | 0.071(1) |
| O3 | −0.3830(6) | 0.5878(3) | 0.5603(5) | 0.082(2) |
| H1 | 0.226(7) | 0.577(3) | 0.410(7) | |
| H2 | 0.117(8) | 0.579(3) | 0.317(6) | |
| H3 | 0.043(8) | 0.552(3) | 0.716(6) | |
| H4 | −0.114(8) | 0.564(4) | 0.692(6) | |
| H5 | 0.198(7) | 0.704(3) | 0.391(6) | |
| H6 | −0.007(8) | 0.690(3) | 0.452(6) | |
| H7 | 0.257(7) | 0.668(3) | 0.604(7) | |
| H8 | 0.141(7) | 0.747(4) | 0.568(6) | |
| H9 | −0.021(8) | 0.681(3) | 0.756(6) | |
| H10 | −0.125(8) | 0.681(3) | 0.614(7) | |

[a] $U_{eq} = 1/3$ (trace of the orthogonalized $U_{ij}$ matrix).

The axial bond length is very similar to that obtained before, 2.557(4) and 2.55(1) Å, respectively. However, the Cu–N bond lengths are seemingly shorter, now 2.011(4) and 2.027(5) Å; previously 2.04(1) and 2.09(1) Å, respectively. The bite angle N1–Cu–N2 is now 93.2(2)° (versus 94.9(5)°). The values are similar to those found for bis(2,2-dimethylpropane-1,3-di-

TABLE 2. Selected bond lengths (Å) and angles (°) for the non-hydrogen atoms of the title compound

| | X-ray | CFF[a] |
|---|---|---|
| Bond lengths | | |
| Cu–N1 | 2.011(4) | 2.020 |
| Cu–N2 | 2.027(5) | 2.020 |
| Cu–O1 | 2.557(4) | 2.557 |
| C1–C2 | 1.500(11) | 1.535 |
| C1–N1 | 1.455(7) | 1.442 |
| C2–C3 | 1.480(12) | 1.535 |
| C3–N2 | 1.462(7) | 1.443 |
| N3–O1 | 1.240(6) | 1.442 |
| N3–O2 | 1.232(6) | 1.140 |
| N3–O3 | 1.212(7) | 1.140 |
| Bond angles | | |
| N1–Cu–N2 | 93.2(2) | 87.3 |
| C2–C1–N1 | 112.8(5) | 111.5 |
| C1–C2–C3 | 116.2(7) | 113.1 |
| C2–C3–N2 | 113 3(5) | 111.5 |
| Cu–N1–C1 | 121.8(4) | 130.0 |
| Cu–N2–C3 | 123.8(4) | 129.6 |
| O1–N3–O2 | 117.5(5) | 119.6 |
| O1–N3–O3 | 120.5(5) | 120.8 |
| O2–N3–O3 | 121.9(5) | 119.5 |
| Cu–O1–N3 | 125.7(3) | 111.2 |

[a] CFF refers to the optimized structure.

TABLE 3. Statistical parameters for the $MO_2tn_2$ complexes

| | $z_1$ (Å) | $z_2$ (Å) | $z_3$ (Å) |
|---|---|---|---|
| Sample size | 25 | 25 | 25 |
| Average | 0.931 | 0.659 | 0.931 |
| Median | 0.984 | 0.735 | 0.986 |
| Variance | 0.028 | 0.076 | 0.029 |
| Standard error | 0.034 | 0.055 | 0.034 |
| Minimum | 0.513 | −0.027 | 0.429 |
| Maximum | 1.135 | 0.942 | 1.104 |
| Range | 0.622 | 0.969 | 0.675 |
| | av. $\langle z_1 z_3 \rangle$ (Å) | Bite size (Å) | Bite angle (°) |
| Sample size | 25 | 25 | 25 |
| Average | 0.931 | 2.880 | 88.50 |
| Median | 0.981 | 2.854 | 87.92 |
| Variance | 0.028 | 5.359E-3 | 3.064 |
| Standard error | 0.034 | 0.015 | 0.350 |
| Minimum | 0.471 | 2.757 | 86.25 |
| Maximum | 1.109 | 3 035 | 92.83 |
| Range | 0.638 | 0 278 | 6.581 |
| | M−N1 (Å) | M−N2 (Å) | av. M−N (Å) |
| Sample size | 25 | 25 | 25 |
| Average | 2.066 | 2.061 | 2.063 |
| Median | 2.049 | 2.041 | 2.042 |
| Variance | 1.780E-3 | 1.751E-3 | 1.724E-3 |
| Standard error | 8.438E-3 | 8.369E-3 | 8.305E-3 |
| Minimum | 1.997 | 1.984 | 1.991 |
| Maximum | 2.126 | 2.125 | 2.121 |
| Range | 0.129 | 0.141 | 0.131 |
| | M−O (Å) | | |
| Sample size | 25 | | |
| Average | 2 351 | | |
| Median | 2.481 | | |
| Variance | 0.048 | | |
| Standard error | 0.044 | | |
| Minimum | 1 898 | | |
| Maximum | 2.665 | | |
| Range | 0.767 | | |

amine)copper(II) dinitrate; 2.029(4), 2.020(3) Å for the Cu–N bond lengths and 92.56(2)° for the bite angle [10].

To get a general view of the conformational properties of the tn chelates, a survey was performed in CSD to find the pseudo octahedral *trans*-bis(tn)M complex units (where M is a metal cation in the transition series with oxygens in the axial positions). Only the compounds with Cu(II), Ni(II) and Co(III) cations were found to form this kind of complex.

Special emphasis was laid on the bite angle, bite size and puckering of the ring. The puckering parameters are defined as in ref. 3: the $z_i$ values describe the distance of a carbon $C_i$ from the corresponding $MN_4$ plane. The statistical details are given in Table 3. The variances for the puckering values and bite size are clearly smaller than for the bite angle. Although the sample is relatively small, $N=25$, the values seem to be normally distributed in the range 85–90°. The average value for the majority of the compounds is 87.8(9)°. There are seemingly four outliers, for which the bite angle is wider than 90°. These are the title compound, DAPRNI* (=*trans*-diaquabis(1,3-diaminopropane)-nickel(II) dinitrate [11], KOTBAW* (=*trans*-diaquabis(1,3-diaminopropane)nickel(II) dipicrate [12] and DAMPNI* (=tris(1,3-diaminopropane)nickel(II)*trans*-diaquabis(1,3-diaminopropane)nickel(II) tetrachloride monohydrate) [13].

*Influence of the axial and equatorial bond lengths*

The concept of MIL (mutual interaction of ligands) comprises dependence of axial and equatorial bond lengths in six-coordinated complexes [14]. In $MN_4O_2$ coordination polyhedra the elongation of the axial M–O bond length should result in compression along the equatorial direction. Any contribution from the angles was not taken into account. As the matter of fact, the bite angles are not dependent on the metal–ligand bond lengths. The axial and equatorial bond lengths are

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*Abbreviation used in CSD.

clearly dependent on the central metal ion, however, thus dividing the population into three classes. The same holds true also for the bite size and the puckering values.

There is, however, clear influence of the equatorial bond length on the bite size and bite angle (Fig. 2(a)). Again the compounds may be divided into three classes according to the central atom. When the equatorial bond length increases, the bite size tends to increase in the order Co < Cu < Ni. There are strong correlations between the bite size and bite angle within the Cu and Ni categories. However, the equatorial bond length does not seem to have any effect within the Cu and Ni classes on the bite values.

The tn chelate ring displays chair conformation in all the compounds. The average value for the difference between $z_1$ and $z_3$ is 0.03(3) Å; the range is from 0 to 0.119 Å. The correlation between the bite angle, the average $z_1z_3$ value and $z_2$ value is shown in Fig. 2(b). There is very strong correlation (0.993) between the average $z_1z_3$ and $z_2$ values. It seems that when the chelate ring becomes flattened, the bite angle also has the tendency to get wider, as expected. However, there is clear variation in the bite angles.

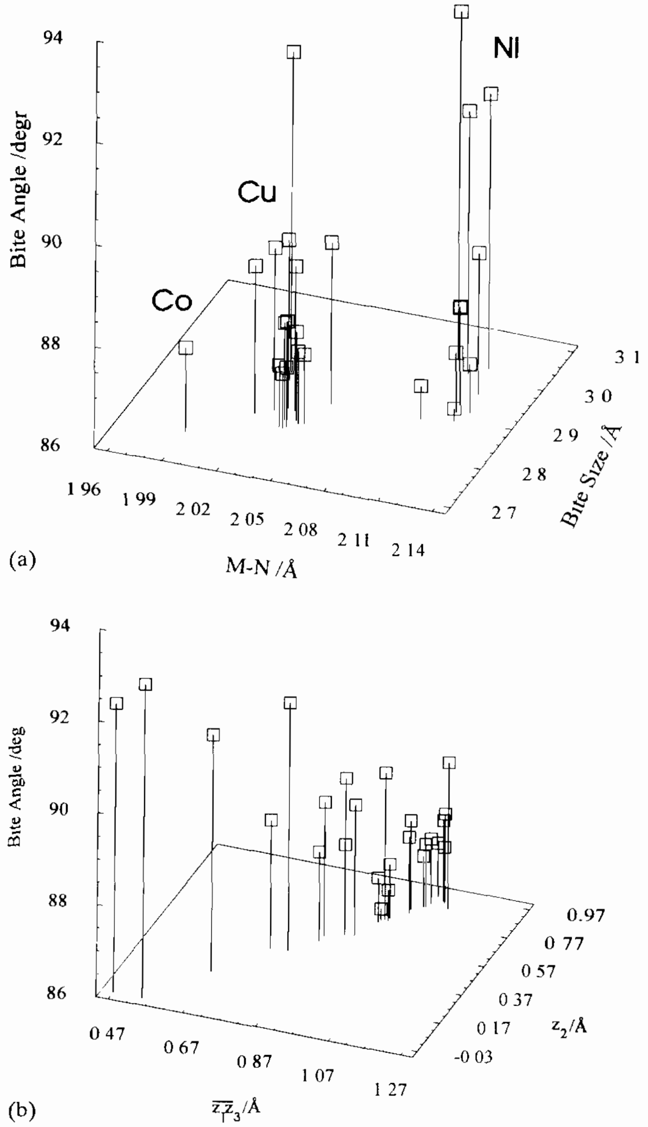

Fig 2. Three-dimensional scatter graphs of the bite angle, equatorial bond lengths, bite size and the puckering values

*Hydrogen bonding*

The value for the bite angle in the title compound remains still quite wide, if we compare it with the values obtained for the other Cu(tn)$_2$ complexes. The energy needed for the deformation is very likely small. Thus intermolecular interactions, and especially hydrogen bonding may very easily have an effect on the bite angle. The hydrogen bonding system is illustrated in Fig. 3 and the respective values are given in Table 4. All the hydrogen bonds are clearly directed outwards from the chelate ring. If we consider these hydrogen bonds as vectors, the sum vector starting from each amino group points outwards. Moreover, there is no intermolecular hydrogen bond to draw the amine nitrogens inwards. If we consider the hydrogen bonding in each compound for which the bite angle is >90°,

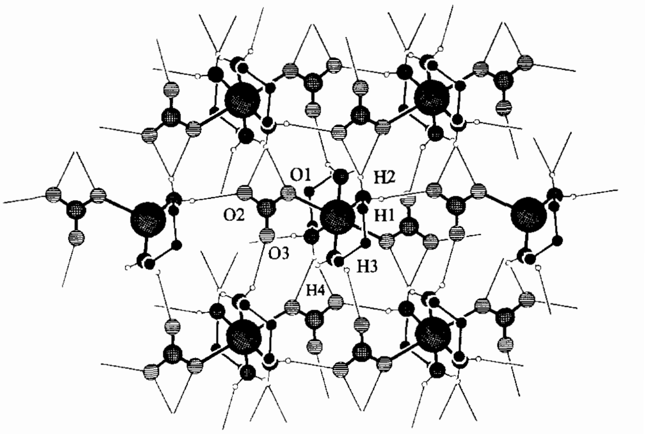

Fig 3. The hydrogen bonding network in *trans*-dinitratobis(1,3-diaminopropane)copper(II). The hydrogen atoms of the methylene groups are omitted for clarity. NB. The hydrogen H4 does not form any hydrogen bond

TABLE 4. Possible hydrogen bonds

| | N–H···O (°) | H···O (Å) | N···O (Å) |
|---|---|---|---|
| N1–H1···O2$^{i}$ | 157(6) | 2.31(6) | 3.065(6) |
| N1–H2···O1$^{ii}$ | 148(6) | 2.37(6) | 3.184(6) |
| N1–H2···O2$^{ii}$ | 156(5) | 2.19(6) | 3.047(6) |
| N2–H3···O3$^{iii}$ | 134(5) | 2.44(6) | 3.092(7) |

Symmetry operators $^{i}1+x, y, z$ $^{ii}\frac{1}{2}+x, y, \frac{1}{2}-z$. $^{iii}\frac{1}{2}+x, y, \frac{3}{2}-z$.

the situation is similar. Either the sum vectors point outwards, or only the equatorial hydrogen in an amine group is hydrogen bonded. In the latter case the vector points clearly outwards.

The Ni(II) analogue DAPRNI has water molecules in the axial positions [11]. The bite angle is wide, 92.9(5)°, even though the nitrate ions are not coordinated. The packing of the nitrate anions is again indicative of outward pulling hydrogen bonding (Fig. 4). Therefore it seems likely that the coordination and subsequent sterical influence of nitrate ion is not playing a decisive role in the widening of the bite angle. In DAMPNI the relevant hydrogen bonding system consists of interactions between chloride ions and the amine groups. Either both of the hydrogen atoms or the equatorial hydrogen are bonded.

Similar hydrogen bonding system is found for KOTBAW, where the hydrogen bonding is formed by the picrate ions. An equatorial hydrogen forms a bifurcated hydrogen bond to a picrate ion.

### *Theoretical calculations*

The chelate ring is clearly less puckered than found in the other complexes so far. The values for $z_1$, $z_2$ and $z_3$ are 0.513(11), $-0.263(12)$ and 0.429(11) Å, respectively. The present compound is the first Cu(II) complex where the central carbon atom of the chelate ring lies on the other side of the $CuN_4$ plane from the other two carbon atoms. Although the values for the present compound are strikingly different, they still seem to belong to the same category as the values found so far. The correlation between the average value $\langle z_1 z_3 \rangle$ and $z_2$ is 0.991 within the Cu(II) category.

The CFF calculations made earlier predicted that the lowest-energy pathway for chair-to-chair interconversion would require a skew-boat conformation for $z_2 = 0$ [3]. However, the observed values for $z_1$ and $z_3$ are very similar and do not show any significant difference, although $z_2$ has a negative value.

CFF calculations were performed to study further the chelate ring properties. The strategy in the course of the optimization was similar to that reported earlier for *trans*-ditosylatobis(1,3-propanediamine)copper(II) [15]. The *trans*-dinitratobis(1,3-diaminopropane)-copper(II) complex was optimized with the central copper atom requiring planar coordination and the Cu–N distances fixed (the force constant had a value of 10000 mdyn/Å) at the average value of 2.019 Å obtained from the observed values. The chelate rings were in chair conformation already in the beginning of the optimization. After the minimization was complete, the nitrate anions were added into axial positions with fixed Cu–O distance of 2.557 Å. The Cu–N distances were kept fixed as before. All the hydrogen atoms connected to the nitrogen atoms were activated to be able to form intramolecular hydrogen bonds during the optimizations. Several different starting positions for the anions always produced a similar configuration.

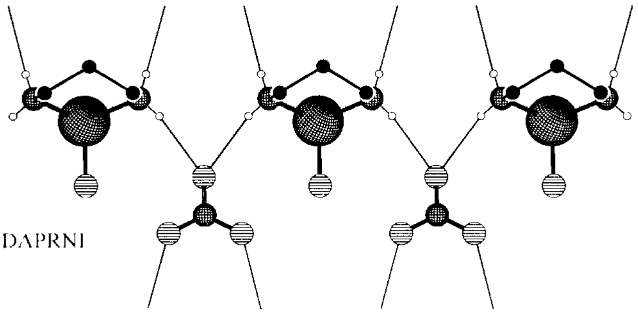

Fig. 4. Part of the hydrogen bonding network in DAPRNI. The hydrogen atoms in the methylene groups as well as the hydrogens of the water molecules are omitted for clarity.

The bond lengths and angles for the optimized structure are given in Table 1. No intramolecular hydrogen bonds were formed between the oxygen and the hydrogen atoms of the amine groups in agreement with the situation in the observed structure. The most prominent differences are seen in the bonding parameters of the nitrate anion. The semiempirical calculations made earlier by Gollogly and Hawkins predict that the bite angle N–Cu–N should be 90° or even wider [3]. The present optimization gives the value of 87.3° which is similar to the value of 87.5° calculated earlier for *trans*-ditosylatobis(1,3-propanediamine)copper(II) [15]. These values are also quite close to the observed values of 87.09(14) and 87.1(1)° found for *trans*-dibenzoatobis(1,3-diaminopropane)copper(II) and *trans*-di(3-iodobenzoato(bis(1,3-diaminopropane)copper(II), respectively [5, 6]. Moreover, the optimized bite angle is very close to the average value of 87.8(9)° for the major population of the structures found from CSD. Because there was only one complex unit included in the optimization, the intermolecular interactions were accordingly excluded. Therefore, the assumption of the importance of hydrogen bonding as a cause for the widening of the bite angle gains indirect support.

To study the electronic properties due to the central copper(II) atom, extended Hückel calculations were performed for a simplified complex unit. It consisted of the Cu(II) cation, four $NH_2$ fragments in the equatorial plane and two axial nitrate anions. The nitrate anions were positioned so that one of the oxygen atoms pointed to a hydrogen connected to an amine nitrogen. Then the two opposite N–Cu–N angles were allowed to vary in the range 86.1–96.1°. The result is shown in Fig. 5. The total energy depicted is in another scale for clarity. Interestingly, there is a minimum corresponding to a bite angle of about 92°. However, the difference between the maximum and minimum value is only 1.23 cal/mol. The widening of the angle does

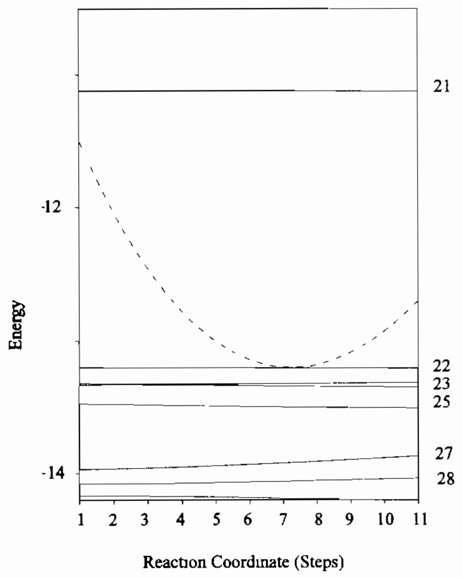

Fig. 5. Walsh diagram depicting the highest occupied molecular orbitals for a $Cu(NH_2)_4(NO_3)_2$ moiety. The reaction coordinate is composed of the bite angles in the range 86.1–96 1°

not affect the HOMO, but instead the molecular orbitals consisting mainly of $d_{xz}$ and $d_{yz}$ orbitals of the Cu(II) ion (MOs 27 and 28, respectively). Because the orbitals consist only of the d orbitals of the central metal ion and the surrounding nitrogen atoms, the effect is qualitatively the same for Cu(II), Ni(II) and Co(III) ions.

However, the overall change of energy is so small that it is overruled by the packing effects, which are usually of the order of 10 kcal/mol. Preliminary *ab initio* calculations performed for an aqua-bis(1,3-diaminopropane)copper(II) cation show that when the bite angle is increased from 90 to 94°, the energy cost is only 0.643 kcal/mol [16].

Another possible explanation for the deviation of the bite angle from the expected value of 90° might be vibronic coupling of the highest occupied molecular orbitals. However, it can be readily shown that if the site symmetry around the copper(II) ion is $D_{4h}$, the distortion modes do not affect the bite angle.

## Supplementary material

Listings of the structure factors, least-square planes and thermal parameters are available from the author.

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