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The structural pathways of (dipicolylamine)dinitratocopper(II): an example of the uncommon see-saw stereochemistry

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The dark blue complex [Cu(dipica)$(NO_3)_2$] (dipica = dipicolylamine, bis(2-pyridylmethyl)amine) has been isolated and characterized by single crystal X-ray crystallography. The five-co-ordinate CuN_3O_2 chromophore is located in a general position and involves a planar tridentate co-ordination of the dipica nitrogen atoms with short Cu–N_{py} [1.965(4), 1.970(5) Å] and Cu–N_{amine} [1.973(6) Å] distances. Both the nitrate ions are co-ordinated in a plane almost perpendicular (90.15°) to the CuN_3 plane with slightly different Cu–O distances [Cu–O(1), 2.153(4); Cu–O(4), 2.148(4) Å] and a O(1)CuO(4) angle of 78.4°. The value of the trigonal index τ of 0.33 [$(a_8 - a_1)/60$, where a_8 = N2–Cu–N1 and a_1 = O1–Cu–N3] suggests that the structure is best described as trigonal bipyramidal distorted square based pyramidal (TBDSBP). Two further remote oxygen atoms of the nitrato ligands are semi-co-ordinated in the CuO(1)O(4) plane with much longer Cu–O′ distances [Cu–O2, 2.698(4); Cu–O6, 2.870(4) Å] so that the complex may be considered alternatively to possess a near seven-co-ordinate $CuN_3O_2O'_2$ chromophore. According to the Structural Pathway of the vibronic coupling model the five-co-ordinate structure is then best described as an extreme see-saw structure which is best understood in terms of a distortion of the regular five-co-ordinate trigonal bipyramidal stereochemistry involving a −A + B route distortion. With an O(1)CuO(4) angle of 78.4° this structure is the most extreme example known of the uncommon see-saw stereochemistry of the copper(II) ion.

Introduction

Five-co-ordinate copper(II) complexes have elicited much interest[1,2] as they display varying co-ordination geometries. More recently a wide range of distorted forms of the cations $[Cu(bipy)_2Cl]^+$ (bipy = 2,2′-bipyridyl),[3] $[Cu(phen)_2Cl]^+$,[4] $[Cu(phen)_2Br]^+$[5] and $[Cu(phen)_2(H_2O)]^{2+}$[6] (phen = 1,10-phenanthroline) have been recognized. In these series the basic five-co-ordinate stereochemistry is clearly intermediate between square based pyramidal and trigonal bipyramidal depending on the anion present and illustrates intermediate forms, each with a static local molecular stereochemistry, in the mechanistic pathway of the Berry Twist[7] from a regular trigonal bipyramidal (RTBP) to a regular square pyramidal stereochemistry (RSBP). The concept of a structural pathway for these complexes has been developed[3] recently to describe these structures in terms of a vibrational coupling model.[8] Thus the structural pathways of the five-co-ordinate $[Cu(bipy)_2Cl]Y$ series of complexes **1** (Fig. 1) have been reported using eighteen structures.[9] In the distortion of RTBP to RSBP stereochemistry the modes of vibration of the in-plane CuN_2Cl portion of the chromophore involved are $\nu_{sym}{}^{str}$, $\nu_{sym}{}^{bend}$, $\nu_{asym}{}^{str}$ and $\nu_{asym}{}^{bend}$ (Fig. 1). These senses of distortion can conveniently be described in terms of the ±A and ±B routes of Fig. 1. The ±A route of distortion solely involves $\nu_{sym}{}^{str}$ and $\nu_{sym}{}^{bend}$ modes of vibration, both of which retain the C_2 symmetry of the CuN_4Cl chromophore. On the other hand, the ±B route of distortion is determined by the $\nu_{asym}{}^{str}$ and $\nu_{asym}{}^{band}$ modes, both of which lower the symmetry of the CuN_4Cl chromophore to C_1. Thus the $[Cu(bipy)_2Cl]X$ series of complexes are described with −A route distortion involving also a significant +B route distortion. The pure −A route distortion with C_2 symmetry is represented by the left horizontal distortion through the RTBP stereochemistry in Fig. 1 and has been used to describe the stereochemistry of the complexes $[Cu(terpy)(NCS)_2]$ **2**[10] and $[Cu(terpy)Br_2]$ **3**[10] where terpy = 2,2′ : 6′,2″-terpyridine, both with C_2 symmetry (Fig. 2) as a *reversed* trigonal bipyramidal[10] (RevTBP), implying that the pure +A route distortion, illustrated by the right horizontal distortion in Fig. 1, is referred to as *normal*. These complexes have the a_3 (XCuX) angles of 98.1(3) (**2**) and 109.0(0)° (**3**), which are near enough to the RTBP angle of 120° to justify them to be described as having RevTBP stereochemistry. On the other hand, the complexes $[Cu(py)_2(ONO_2)_2]$ **4**[11] (py = pyridine) and $[Cu(hfacac)_2(NH_3)]$ **5**[12] (Fig. 2, Hhfacac = 1,1,1,5,5,5-hexafluoroacetylacetone) are known to possess even lower angles of 91.4(3) and 90.8(2)° respectively. As the a_3 angles are nearly 30° less than the 120° of the RTBP stereochemistry, it is inappropriate to describe them as RevTBP and so the term *see-saw* distorted trigonal bipyrimidal (SSDTBP) has been introduced to describe their geometries;[9] however, it should be noted that the distinction between these two geometries is only arbitrary.

The present report describes the preparation, crystal structure determination and spectroscopic properties of the complex [Cu(dipica)$(NO_3)_2$] (dipica = dipicolylamine, *i.e.* bis(2-pyridylmethyl)amine) with an even lower a_3 (OCuO) angle of 78.4° and a slight rhombic distortion away from C_2 symmetry.

Experimental

Materials

All reagents for syntheses were used as received from Aldrich Chemicals or Fluka. 2,2′-Dipicolylamine [bis(2-pyridylmethyl)amine] was a gift from Reilly Industries.

(Dipicolylamine)dinitratocopper(II), [Cu(dipica)$(NO_3)_2$]

This compound was prepared by the addition of a methanolic solution (5 mL) of $Cu(NO_3)_2$ (0.199 g, 1 mmol) to a solution of

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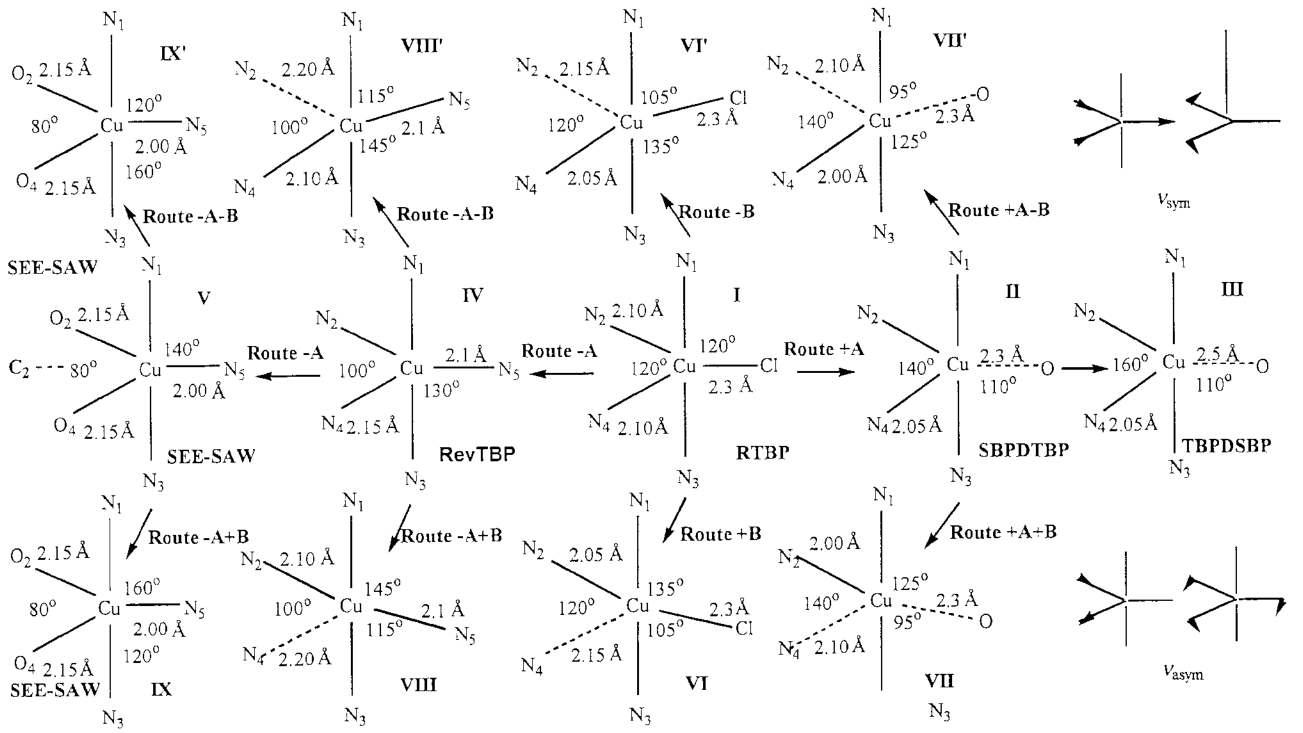

Fig. 1 Full structural pathways of the CuN_4X chromophore involving the A, B and A + B route distortions. The bond distances have been rounded off to the nearest 0.05 Å and the bond angles to the nearest 5°.

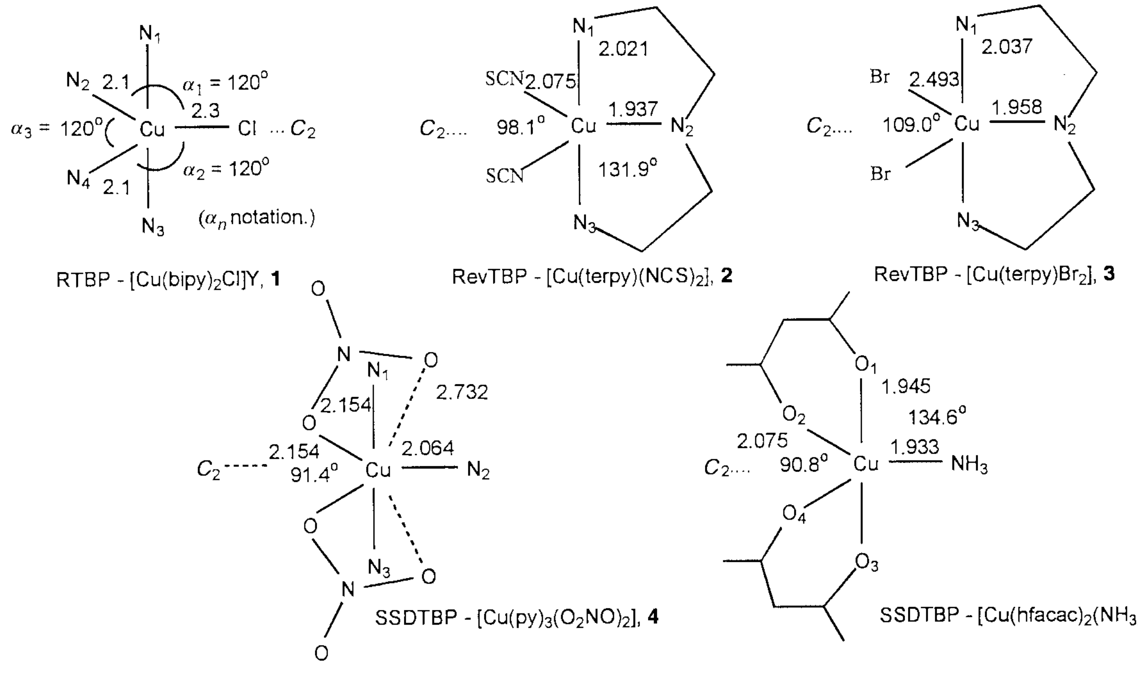

Fig. 2 Molecular structures 1–5.

dipica (0.199 g, 1 mmol) in methanol (10 mL) with stirring, and then allowing the solution to evaporate slowly at room temperature. The dark blue crystals of the nitrate, which were deposited after a few days, were suitable for X-ray diffraction. Yield 0.35 g, 90%. Calc. for $C_{12}H_{13}CuN_5O_6$: C, 37.26; H, 3.39; N, 18.11. Found: C, 36.84; H, 3.41; N, 18.08%.

Physical measurements

Elemental analyses were performed at CDRI, Lucknow, India. The diffuse-reflectance spectrum was measured on a Hitachi U-3400 double-beam UV/VIS-NIR spectrophotometer and the EPR spectrum on a Varian E 112 X-band spectrometer calibrated with diphenylpicrylhydrazyl (dpph).

Crystal structure determination

A dark blue crystal of $[Cu(dipica)(NO_3)_2]$ was mounted within thin-wall capillaries. Intensity measurements were performed on a Siemens P4-four circle diffractometer equipped with a conventional molybdenum X-ray source, graphite monochromator and scintillation counter. The lattice parameters of the monoclinic cell were derived from 30 carefully centered orientation reflections taken from a rotation photograph. Intensity data were collected by the ω–2θ scan technique. In both cases two octants of data (in addition to the $h = -1$ shell) were collected implying the restriction of C-centering. The data reduction involved Lorentz and polarization corrections,[13] as well as an empirical absorption correction using

Table 1 Crystallographic data for [Cu(dipica)(NO$_3$)$_2$] **1**

Chemical formula	$C_{12}H_{13}CuN_5O_6$
M	386.81
Space group	$C2/c$ (monoclinic, no. 15)
a/Å	14.853(4)
b/Å	8.050(1)
c/Å	25.395(4)
β/°	103.18(2)
V/Å^3	2956(1)
Z	8
T/°C	20
λ(Mo-Kα)/Å	0.71073
ρ_{calc}/g cm^{-3}	1.738
μ/cm^{-1}	7.6
Independent reflections	3195 (R_{int} = 0.0345)
Reflections with $I > 2.00\ \sigma(I)$	2278
R	0.0573
R_w	0.0613

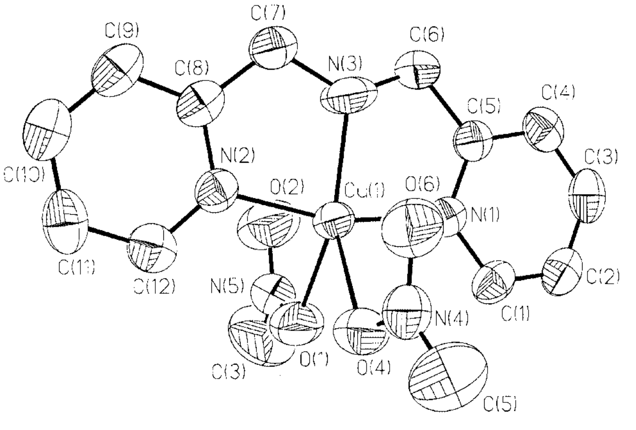

Fig. 3 An ORTEP drawing of [Cu(dipica)(NO$_3$)$_2$] showing the atom numbering and thermal motion ellipsoids (50% probability level) for non-hydrogen atoms.

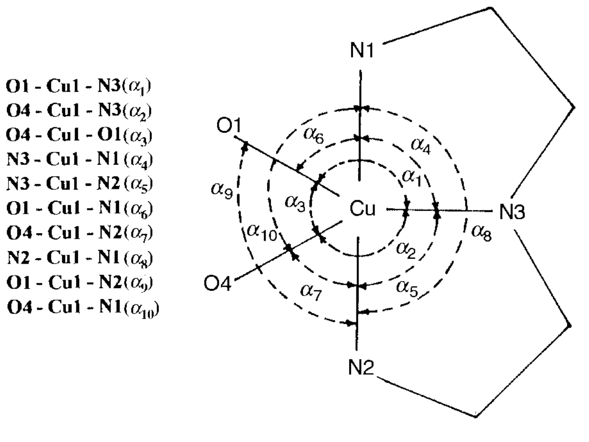

Fig. 4 The angular notation (a_n) used to illustrate the [Cu(dipica)(NO$_3$)$_2$] structure.

3 ψ-scan reflections. Initial structural models (Cu, O, N, and some C) were obtained by direct methods (SHELXTL program package).[14] The remaining C atoms were obtained from Fourier-difference maps following some least-squares cycles. After isotropic refinement of these models H atoms were added on idealized positions. One common isotropic thermal parameter per group was refined for the riding H atoms. Details of the data collections, structure solutions and refinements are given in Table 1 and important bond lengths and angles in Table 2.

CCDC reference number 186/1849.

See http://www.rsc.org/suppdata/dt/a9/a908185b/ for crystallographic files in .cif format.

Table 2 Selected bond distances and angles for [Cu(dipica)(NO$_3$)$_2$][a]

Cu–N1	1.965(4)	Cu–O4	2.148(4)
Cu–N2	1.970(5)	Cu–O2	2.698(4)
Cu–N3	1.973(6)	Cu–O6	2.870(4)
Cu–O1	2.153(4)		
O1–Cu1–N3 (a_1)	145.3(3)	O1–Cu1–N1 (a_6)	94.0(2)
O4–Cu1–N3 (a_2)	136.3(3)	O4–Cu1–N2 (a_7)	97.7(2)
O4–Cu1–O1 (a_3)	78.4(2)	N2–Cu1–N1 (a_8)	164.8(2)
N3–Cu1–N1 (a_4)	82.4(3)	O1–Cu1–N2 (a_9)	97.2(2)
N3–Cu1–N2 (a_5)	82.5(3)	O4–Cu1–N1 (a_{10})	94.6(2)

[a] Distances in Å, angles in °, and standard deviation in last significant digit in parentheses.

Results and discussion

Structure of [Cu(dipica)(NO$_3$)$_2$]

An ORTEP[15] plot of the local molecular structure of the complex [Cu(dipica)(NO$_3$)$_2$] is illustrated in Fig. 3 along with the atom numbering scheme. The reduced angle notation (a_n) is shown in Fig. 4, corresponding to that used for the RTBP stereochemistry (Fig. 1). The structure of the complex molecule involves a five-co-ordinate CuN_3O_2 chromophore with a trigonal bipyramidal co-ordination environment. The tridentate dipica ligand bonds in a planar conformation with its two pyridine nitrogen atoms occupying the axial positions. The oxygen atoms O1 and O4 of the nitrato ligands are co-ordinated in a plane at right angles (90.15°) to the dipica plane, at almost the same Cu–O distance [Cu–O(1), 2.153(4); Cu–O(4), 2.148(4) Å] as expected. It is interesting that the mutually *trans* out-of-plane Cu–N$_{py}$ distances [1.965(4), 1.970(5) Å] and the single in-plane Cu–N$_{amine}$ distance [1.973(6) Å] are almost equal and short. Generally the M–N$_{het}$ distance is shorter than the M–N$_{amine}$ distance, as observed in six-co-ordinate [Cu(dipica)$_2$][BF$_4$]$_2$,[16] [Cu(bba)Cl$_2$][bba = bis(benzimidazol-2-ylmethyl)amine],[17] [Cu(bba)$_2$][ClO$_4$]$_2$,[18] [Cu$_2$(tpbd)(H$_2$O)$_4$][S$_2$O$_6$]$_2$[tpbd = *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)benzene-1,4-diamine],[19] [Fe(dipica)Cl$_3$],[20] and [Fe(dipica)$_2$]$^{2+}$[21] complexes on account of the difference in hybridization of the nitrogen atoms. In the present complex the observed short Cu–N$_{amine}$ distance probably results from the small bite angles [a_4, 82.4(3); a_5, 82.5(3)°] of the dipica ligand. A similar observation has been made for the five-co-ordinate square pyramidal [Cu(dipica)$_2$][BF$_4$]$_2$ complex[16] in which the axial Cu–N$_{py}$ distance (2.044 Å) is longer than the equatorial Cu–N$_{amine}$ distance (1.995 Å). Further, the in-plane a_1, a_2 and a_3 angles (145.3, 136.3, 78.4°), sum 360°, deviate from the value of 120° expected for the RTBP geometry. The out-of-plane a_4 and a_5 angles are less and the out-of-plane a_6, a_7, a_9 and a_{10} angles greater than the expected RTBP angles of 90°. The a_8 angle is 164.8(2)°, which is clearly less than 180° due to the small bite angles (a_4, a_5) of the dipica ligand. The angle between the CuN$_3$ and CuO$_2$ planes of 90.15° is very close to 90°, with the remaining atoms of the nitrato groups lying close to the CuO$_2$ plane. These distortions and the value of the trigonal index τ[22] [$= (a_8 - a_1)/60$] of 0.33 suggest that the structure is best described as trigonal bipyramidal distorted square based pyramidal[4] (TBDSBP). While both the nitrate anions are co-ordinated in our complex, only one is co-ordinated in the benzimidazole (bzim) analog [CuL(NO$_3$)]NO$_3$ [L = bis(benzimidazolylmethyl)-n-butylamine] and its homologs,[23] obviously because of the bulkiness of the bzim moiety which prevents the other nitrate anion from co-ordination. If the remote O(2) and O(6) oxygen atoms of the nitrato groups at longer distances [Cu–O(2), 2.698(4); Cu–O(6), 2.870(4) Å] are considered to be involved in semi-co-ordination, then the structure would correspond alternatively to a seven-co-ordinate $CuN_3O_2O'_2$ chromophore. While the two short Cu–O(1) and Cu–O(4) distances hardly show significant difference, the Cu–O(2) and

Cu–O(6) distances are clearly different and hence lower the symmetry of the $CuN_3O_2O'_2$ chromophore from C_2 to C_1. This lowering is supported by the asymmetry in the values of the N(3)CuO(1) (a_1) and N(3)CuO(4) (a_2) angles.

The five-co-ordinate structure of our complex is closely comparable to the very rare five-co-ordinate copper(II) complexes like $[Cu(terpy)(NCS)_2]$ **2**,[10] $[Cu(terpy)Br_2]$ **3**[10] and $[Cu(py)_3(O_2NO)_2]$ **4**,[11] all of which involve a crystallographic twofold axis and show an extreme see-saw stereochemistry (−A route distortion), but differs in two respects. First the copper(II) ions in these complexes lie on a crystallographic twofold axis of symmetry and secondly their a_3 angles [**2**, 98.1; **3**, 109.0; **4**, 91.4°] are significantly higher than that (78.4°) of our complex. These complexes can be considered to undergo a pure −A route distortion (Fig. 1) and so are appropriately described as having a RevTBP stereochemistry as their a_3 angles are within 29° of 120° of a RTBP stereochemistry. On the other hand, the a_3 angles of the present complex, **4** and $[Cu(hfacac)_2(NH_3)]$ **5**[12] are significantly less than 120°, with that of the present complex being more than 40° less; so it is inappropriate to describe the stereochemistry of these three complexes as RevTBP. Moreover, the in-plane Cu–O(1) and Cu–O(4) distances of our complex and **4** of *ca.* 2.15 Å are considerably longer than that of 2.10 Å normally associated with the in-plane Cu–O/N distances of the RTBP stereochemistry. On these grounds the basic stereochemistry of the present complex and of **4** and **5** is significantly different from those of **2** and **3** and hence deserves a separate description as SEE-SAW RTB (SSRTB).[9]

The stereochemistries of **4** and **5** differ from that of our complex in having a crystallographic twofold axis of symmetry and hence described as having a pure −A route distortion, which involves the pure $\nu_{sym}{}^{str}$ and $\nu_{sym}{}^{bend}$ modes of vibration. The distorted CuN_3O_2 chromophore of the present complex with slight contraction along the Cu–N(3) distance (opposite to a_3), the almost equal Cu–N(1) and Cu–N(2) distances and the non-equivalence of a_1 and a_2 angles without a twofold axis of symmetry is considered to involve the −A + B route distortion with the obvious domination of −A over +B, involving all the four modes of vibration $\nu_{sym}{}^{str}$, $\nu_{sym}{}^{bend}$, $\nu_{asym}{}^{str}$ and $\nu_{asym}{}^{bend}$, namely the molecular structures IX and IX′ of Fig. 1. Alternatively, the precise co-ordination geometry displayed may be interpreted[5] as an effect of vibronic coupling of a linear combination of the nuclear modes of vibrations ν_{sym}, a symmetric C_2 mode, and ν_{asym}, an asymmetric non-C_2 mode, of the CuN_3O_2 chromophore.

Electronic properties

The polycrystalline EPR spectrum of the complex is clearly axial, suggesting a $d_{x^2-y^2}$ ground state for Cu^{II}. The axial g values of 2.097 and 2.207 correspond to crystal g values and not the local molecular g values because of misalignment of the local molecular axes. However, in view of the short N(1)Cu(N2) distances in the complex, a d_{z^2} ground state is the more likely, as already established for the related complex **4** by single crystal EPR measurements. The polycrystalline electronic spectrum of the complex displays only one ligand field band around 15 300 cm^{-1}. It is difficult to assign this band as the ground state could not be confirmed.

Conclusion

The present report describes the preparation, crystal structure determination and spectroscopic properties of the 1:1 copper(II) nitrate complex of dipicolylamine. The crystal structure of the complex $[Cu(dipica)(ONO_2)_2]$ with low symmetry CuN_3O_2 chromophore involves a five-co-ordinate see-saw stereochemistry with an extreme O(1)CuO(4) (a_3) angle of 78.4° and a slight rhombic distortion away from C_2 symmetry. We have invoked the involvement of vibronic coupling (−A + B route distortion) to account for the observed structure. The ability of the dipica ligand to co-ordinate to copper(II) in a planar conformation is also demonstrated.

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