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Non-Thermochromic Bis(*N,N*-dimethylethylenediamine)copper(II) Dinitrate

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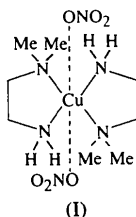
Abstract

Non-thermochromic bis(*N,N*-dimethylethylenediamine)-copper(II) dinitrate, [Cu(C₄H₁₂N₂)₂](NO₃)₂, has been investigated by single-crystal X-ray diffraction methods. The Cu²⁺ ion has a tetragonally distorted octahedral environment, where four N atoms of the two ligand molecules are equatorial [Cu—N1 2.082 (2) and Cu—N2 1.992 (2) Å] and two O atoms of the NO₃[−] ions are axial [Cu···O2 2.765 (2) Å]. The non-thermochromic behaviour is explained in terms of stronger Cu–axial interactions and hydrogen bonding by the anions, compared with those of their homologous thermochromic counterparts.

Comment

Although it has been known for a long time that Cu complexes with *N,N*-dialkyl-substituted ethylenediamine ligands exhibit thermochromic behaviour (Pfeifer & Glaser, 1938), only one example, [Cu{*asym*-(C₂H₅)₂en}][ClO₄]₂, has been investigated above (blue) and below (red) its transition temperature using X-ray crystallographic techniques (Grenthe, Paoletti, Sandstrom & Glikberg, 1979). These studies revealed that the colour change was not due to a change in axial interaction, as widely believed previously (Lever, Mantovani & Donini, 1971; Lever & Mantovani, 1971), but rather the result of dynamic disorder of the chelate-ring atoms, suggested only by Hatfield, Piper & Klabunde (1963) 16 years prior to the X-ray studies. The title compound, (I), was studied in order to examine the effects of both *N,N*-dialkyl substitution and the presence of a counterion on thermochromic behaviour.

The coordination geometry around the Cu atom is tetragonally distorted octahedral. The Cu atom is at the crystallographic centre of symmetry with the four



N atoms of the two ethylenediamine moieties in a plane [Cu—N1 2.082 (2) and Cu—N2 1.992 (2) Å] and the two NO₃[−] ions involved in weak axial coordination through their O2 atoms [Cu···O(2) 2.765 (2) Å] (Fig. 1). The axial Cu···O distance of the title complex is between that of [Cu(*N,N'*-dimethylethylenediamine)₂](NO₃)₂ [Cu···O_{nitrate} 2.506 (8) Å; Koner, Ghosh & Chaudhuri, 1993] and that of [Cu(*N,N*-diethylethylenediamine)₂](NO₃)₂ (red) [Cu···O_{nitrate} 4.192 (3) Å; Beena & Bhadbhade, 1995]. The variation in the Cu–anion interaction in these complexes can be rationalized on the basis of the steric factors associated with the *N*-alkyl substituents. The shortening of the Cu—N2 distance compared to Cu—N1 is significant and also observed for [Cu(*N*-methylethylenediamine)₂](NO₃)₂ (Luukkonen & Pajunen, 1969). The C1—C2 bond length [1.501 (4) Å] in (I) is slightly shorter than the accepted C_{sp³}—C_{sp³} bond length (1.537 Å). A very large decrease, *i.e.* from 1.507 (5) Å in the red form to 1.37 (2) Å in the blue form, has been noted for [Cu(*N,N*-diethylethylenediamine)₂](ClO₄)₂ as a result of dynamic disorder in the ethylenediamine C atoms at high temperature. However, thermal anisotropies of atoms C1 and C2 in compound (I) are within the normal range and do not suggest any disorder. No colour change was observed in the title complex on going from the liquid-nitrogen temperature (77 K) to 423 K and no response was observed in the calorimetric studies over the temperature range used (243 → 423 K and 423 → 243 K). This confirms the non-thermochromic nature of the complex.

A few striking differences in the molecular packing of compound (I) compared with the thermochromic complexes were noted. The molecular packing of

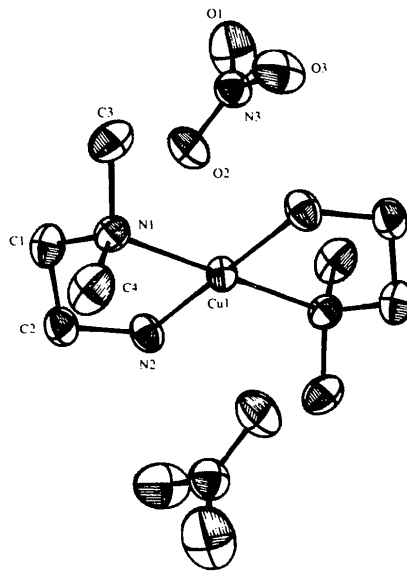


Fig. 1. Perspective view of the title compound shown with 50% probability ellipsoids. H atoms are omitted for clarity.

(I) exhibits stronger axial anionic interactions than thermochromic $[\text{Cu}\{\text{asym}-(\text{C}_2\text{H}_5)_2\text{en}\}_2]\text{X}_2$ systems; the $\text{Cu}\cdots\text{O}_{\text{nitrate}}$ distance in (I) is 2.765 (2) Å, whereas the corresponding distance for $X = \text{NO}_3$ (Beena & Bhadbhade, 1995) is 4.192 (6) Å, for $X = \text{ClO}_4$ (Grenthe *et al.*, 1979) is 3.65 (1) Å (red) and 4.16 (2) Å (blue), and the $\text{Cu}\cdots\text{F}$ distance for $X = \text{BF}_4$ (Beena & Bhadbhade, 1995) is 3.626 (6) Å.

Intermolecular hydrogen bonding exists between the amino N atoms (N2) and the O atoms of the nitrate groups in (I), with the strongest interactions being $\text{N2}\cdots\text{H2N2}\cdots\text{O2}(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2})$ [$\text{N2}\cdots\text{O2}$ 3.123 (3) Å, $\text{N2}\cdots\text{H2N2}\cdots\text{O2}$ 151.4 (1), $\text{H2N2}\cdots\text{N2}\cdots\text{O2}$ 19.8 (1)°]. Moderate to weaker $\text{N2}\cdots\text{H2N2}\cdots\text{O1}$ and $\text{N2}\cdots\text{H1N2}\cdots\text{O3}$ interactions also occur. This is in contrast to the thermochromic complexes which contain no strong hydrogen bonds and have fairly large intermolecular contact distances. Also, the ethylenediamine ring conformation is a rather deep envelope in (I) (atom C1 is displaced by 0.53 Å from the plane containing $\text{N1}\text{—}\text{Cu}\text{—}\text{N2}$), whereas in the thermochromic complexes, atoms C1 and C2 are displaced equally by about 0.30 Å in opposite directions from the $\text{N}\text{—}\text{M}\text{—}\text{N}$ plane. These features could be looked at as the 'non-readiness' of compound (I) to exhibit the dynamic disorder responsible for the thermochromic transition.

Experimental

The synthesis of bis(*N,N*-dimethylethylenediamine)copper(II) dinitrate was carried out in ethanol by the reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and *N,N*-dimethylethylenediamine (molar ratio 1:2). Crystals were obtained by slow evaporation from ethanol.

Crystal data

$[\text{Cu}(\text{C}_4\text{H}_{12}\text{N}_2)_2](\text{NO}_3)_2$
 $M_r = 363.9$
 Monoclinic
 $C2/c$
 $a = 10.099$ (3) Å
 $b = 15.040$ (4) Å
 $c = 9.917$ (2) Å
 $\beta = 98.05$ (2)°
 $V = 1491.4$ (4) Å³
 $Z = 4$
 $D_x = 1.620$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 12\text{--}16^\circ$
 $\mu = 1.50$ mm⁻¹
 $T = 293$ K
 Plate
 $0.48 \times 0.14 \times 0.05$ mm
 Deep blue

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
 $T_{\text{min}} = 0.826$, $T_{\text{max}} = 0.999$
 1302 measured reflections
 1302 independent reflections

1124 observed reflections
 $[I > 3\sigma(I)]$
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 17$
 $l = -11 \rightarrow 11$
 3 standard reflections
 frequency: 60 min
 intensity decay: < 1%

Refinement

Refinement on F
 $R = 0.030$
 $wR = 0.055$
 $S = 1.75$
 1124 reflections
 94 parameters
 H-atom parameters not refined

$w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.08$ e Å⁻³
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cu1	1/4	1/4	1/2	2.058 (9)
O1	0.3180 (3)	0.3455 (2)	0.9564 (3)	5.53 (6)
O2	0.3341 (2)	0.2697 (2)	0.7759 (3)	4.21 (5)
O3	0.1481 (2)	0.3311 (2)	0.8037 (2)	4.93 (6)
N1	0.2840 (2)	0.3812 (2)	0.4474 (2)	2.31 (4)
N2	0.0623 (2)	0.2894 (2)	0.5038 (2)	2.63 (4)
N3	0.2660 (2)	0.3154 (2)	0.8462 (2)	3.00 (5)
C1	0.1484 (3)	0.4156 (2)	0.3914 (3)	3.14 (6)
C2	0.0484 (3)	0.3860 (2)	0.4808 (3)	2.98 (6)
C3	0.3727 (3)	0.3923 (2)	0.3434 (3)	3.48 (6)
C4	0.3407 (4)	0.4325 (2)	0.5694 (3)	3.81 (7)

Table 2. Selected geometric parameters (Å, °)

Cu1—N1	2.082 (2)	N1—C4	1.481 (4)
Cu1—N2	1.992 (2)	N2—C2	1.475 (4)
N1—C1	1.497 (4)	C1—C2	1.501 (4)
N1—C3	1.468 (4)		
O2 \cdots Cu1—N1	96.19 (8)	C1—N1—C3	108.6 (3)
O2 \cdots Cu1—N2	96.35 (8)	C1—N1—C4	110.7 (2)
N1—Cu1—N2	85.05 (9)	C3—N1—C4	108.1 (2)
Cu1—N1—C1	104.3 (2)	Cu1—N2—C2	111.1 (2)
Cu1—N1—C3	115.0 (2)	N1—C1—C2	109.5 (2)
Cu1—N1—C4	110.3 (2)	N2—C2—C1	109.1 (2)

The structure was solved by the heavy-atom method and refined by full-matrix least squares. Computer programs used: *CAD-4 Software* (Enraf–Nonius, 1989) and *SDP* (B. A. Frenz & Associates, Inc., 1985).

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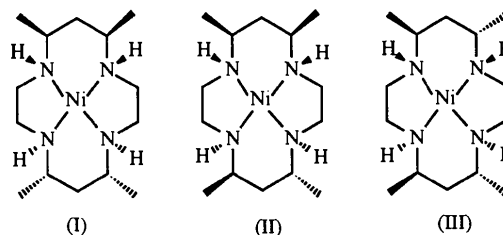
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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complex, (I), with perchlorate has been reported (Hay *et al.*, 1982). This paper reports the crystallization and structure of complex (II).



Two molecules, *A* with coordinates (x_A, y_A, z_A) and *B* with coordinates near ($\frac{1}{2} - x_A, y_A, -\frac{1}{2} + z_A$), of the title complex cation are located in the asymmetric unit. The Ni²⁺ ion has square-planar coordination with the four N atoms of the macrocyclic ligand. These N atoms are coplanar within ± 0.054 (5) Å. The quadridentate ligand has the configuration 1*RS*,4*RS*,8*SR*,11*SR* for the four chiral N-atom centres. The two five-membered chelate rings are in skew forms and the two six-membered chelate rings are in chair forms. The Ni—N distances are close to the average Ni—N distance of 1.95 (4) Å for four-coordinate Ni^{II} macrocyclic complexes (Lu, Chung & Ashida, 1991). In both molecules *A* and *B* of the diastereoisomer (II) and in all three molecules of the diastereoisomer (I) (Hay *et al.*, 1982), the conformations of the 14-membered rings are similar.

All four perchlorate groups are disordered. The amino groups form hydrogen bonds with perchlorate O atoms.

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[(5*SR*,7*RS*,12*RS*,14*RS*)-5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradecane]-nickel(II) Diperchlorate

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Abstract

Two pseudosymmetrically related Ni^{II} complexes are located in the asymmetric unit of solid [Ni(C₁₄H₃₂N₄)]-(ClO₄)₂. The Ni²⁺ ion displays square-planar coordination with the four N atoms of the macrocyclic ligand. The quadridentate ligand adopts its stable conformation with two six-membered chelate rings in chair forms and two five-membered chelate rings in skew forms. The complex has a 1*RS*,4*RS*,8*SR*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,7*RS*,12*RS*,14*RS* configuration for the four chiral C-atom centres.

Comment

According to a previous report (Hay, Jeragh, Ferguson, Kaitner & Ruhe, 1982), the reduction of *C-meso*-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene can give three diastereoisomeric tetraamines and their Ni^{II} complexes, in which the 1*RS*,4*RS*,8*SR*,11*SR* arrangement of the chiral N-atom centres should be as indicated by (I), (II) and (III). The crystal structure of the two isomers of the nickel(II)

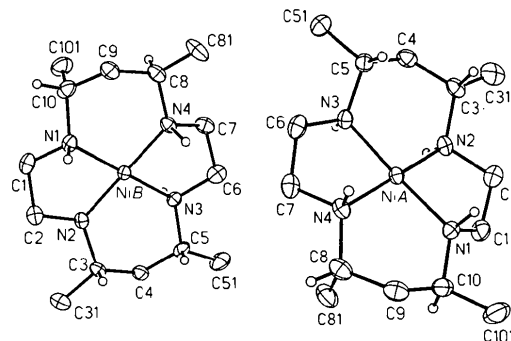


Fig. 1. A perspective view of the two crystallographically independent complex cations, *A* and *B*. The displacement ellipsoids are shown at the 50% probability level (Sheldrick, 1987). Perchlorate anions and selected H atoms are excluded for clarity.

Experimental

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared according to the reported method (Hay & Jeragh, 1977). The ligand contains two chiral C-atom centres. The preparation and separation of nickel(II) complexes of the two diastereoisomers, *C-meso*- and *C-rac*-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-