is little energy difference between the possible configurations. The observed configuration is compared with the calculated $\delta\lambda$ minimum in Fig. 3. Configurations in which one en ring has an envelope conformation are approximately 21 kJ mol^{-1} higher in energy. The thermal parameters of the en C atoms are not large enough to be due either to interconversion between conformations or to a statistical distribution of different conformers in the crystal. The calculations do, however, indicate that for either λ or δ configurations of either ring the energy surface near the minimum is very shallow.

Fig. 4 shows, for en ring II (in the $\delta\lambda$ configuration), the energy for slightly differing conformations. This shallow energy minimum is believed to be responsible for the large libration of the en C atoms in the title compound and it seems likely that similar arguments apply to other Co^{III} (en)$_2$L$_2$ systems when L$_2$ is not too bulky.

The perchlorate ions are poorly determined, the O atoms exhibiting large anisotropic thermal parameters. In consequence the Cl—O lengths (Table 2), being uncorrected for thermal vibration, are shorter than expected. The perchlorate ions and the water molecules are involved in hydrogen-bonding interactions as listed in Table 3 and marked on Fig. 2.

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Amminel 1-(2-hydroxyphenyl)-3,5-diphenylformazanato]copper(II), $C_{19}H_{17}Cu^{II}N_5O$, and Amminel 1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II), $C_{19}H_{17}N_5Ni^{II}O$

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Abstract

$C_{19}H_{17}Cu^{II}N_5O$ is monoclinic, $P2/n$, $a = 24 \cdot 231$ (4), $b = 6 \cdot 5223$ (5), $c = 11 \cdot 449$ (2) Å, $\beta = 90 \cdot 30$ (3)°, $Z = 4$. $C_{19}H_{17}N_5Ni^{II}O$ is triclinic, $P\bar{1}$, $a = 6 \cdot 096$ (3), $b = 12 \cdot 10$ (4), $c = 13 \cdot 60$ (5) Å, $\alpha = 115 \cdot 2$ (3), $\beta = 94 \cdot 3$ (2), $\gamma = 93 \cdot 4$ (3)°, $Z = 2$. The structures were refined to final R values of $4 \cdot 8\%$ for 2788 significant reflections and $4 \cdot 7\%$ for 2029 significant reflections respectively. Both structures have similar approximately square coordination of the metal atoms in which the two outer N atoms of the formazan part, the O atom of the phenyl group and the N atom of the NH$_3$ molecule are involved. The structures consist of columns of similarly stacked units which are packed in a slightly different manner in the two structures.

Introduction

As part of a study on coordination of multidentate ligands with various donor atoms and the role of complex formation in metal-ion oxidation the structures of ammine[1-(2-hydroxyphenyl)-3,4-diphenylformazanato]copper(II) (CUFORM) and of the analogous Ni^{II} complex (NIFORM) are reported. The coordination of the metal ion is indispensable information for constructing mechanistic schemes for complex formation (Balt & Renkema, 1977a).

Experimental

CUFORM

CUFORM was prepared by the procedure of Balt & Renkema (1977b). Usually this results in a microcrystalline powder. After many attempts some larger crystals suitable for single-crystal X-ray work were obtained. These had a slightly higher O content than the microcrystalline product (4·87 against 4·05%).

Crystals of CUFORM are monoclinic, space group $P2/n$, with $a = 24·231$ (4), $b = 6·5223$ (5), $c =$

Table 1. *Fractional coordinates with e.s.d.'s in parentheses*

	CUFORM (M = Cu)			NIFORM (M = Ni)		
	x	y	z	x	y	z
M	0·22431 (2)	0·09997 (10)	0·42132 (6)	0·2715 (1)	0·3720 (1)	0·5597 (1)
C(1)	0·1754 (2)	−0·3135 (7)	0·5355 (4)	0·7050 (8)	0·2936 (4)	0·6418 (4)
C(2)	0·1537 (2)	−0·4958 (8)	0·5981 (4)	0·9000 (8)	0·2540 (4)	0·6827 (4)
C(3)	0·0963 (2)	−0·5383 (9)	0·5963 (5)	0·9815 (10)	0·3100 (5)	0·7934 (4)
C(4)	0·0769 (2)	−0·7088 (10)	0·6574 (6)	1·1654 (10)	0·2715 (6)	0·8306 (4)
C(5)	0·1110 (3)	−0·8327 (10)	0·7200 (6)	1·2708 (10)	0·1787 (5)	0·7619 (5)
C(6)	0·1682 (3)	−0·7959 (9)	0·7198 (6)	1·1943 (9)	0·1227 (5)	0·6520 (5)
C(7)	0·1878 (3)	−0·6262 (9)	0·6597 (5)	1·0119 (9)	0·1610 (5)	0·6128 (4)
C(8)	0·1111 (2)	0·0924 (7)	0·3821 (4)	0·3465 (8)	0·5183 (4)	0·7797 (4)
C(9)	0·1328 (2)	0·2664 (8)	0·3244 (4)	0·1536 (9)	0·5475 (5)	0·7412 (4)
C(10)	0·0953 (3)	0·3978 (9)	0·2682 (5)	0·0361 (9)	0·6366 (5)	0·8148 (5)
C(11)	0·0393 (3)	0·3557 (11)	0·2695 (6)	0·1115 (11)	0·6921 (6)	0·9241 (5)
C(12)	0·0189 (3)	0·1859 (11)	0·3292 (6)	0·3071 (11)	0·6616 (6)	0·9633 (4)
C(13)	0·0544 (2)	0·0548 (10)	0·3839 (5)	0·4255 (9)	0·5749 (5)	0·8921 (4)
C(14)	0·3157 (2)	−0·1747 (7)	0·4956 (4)	0·4276 (8)	0·1880 (5)	0·3743 (4)
C(15)	0·3386 (3)	−0·2724 (9)	0·5907 (5)	0·3228 (10)	0·0715 (5)	0·3331 (5)
C(16)	0·3956 (3)	−0·2961 (10)	0·5979 (6)	0·2735 (12)	0·0026 (6)	0·2224 (5)
C(17)	0·4294 (3)	−0·2257 (11)	0·5112 (6)	0·3360 (12)	0·0491 (6)	0·1519 (5)
C(18)	0·4062 (2)	−0·1286 (10)	0·4143 (6)	0·4427 (11)	0·1655 (6)	0·1919 (5)
C(19)	0·3493 (2)	−0·1033 (7)	0·4055 (5)	0·4877 (10)	0·2346 (5)	0·3032 (4)
N(1)	0·1524 (2)	−0·0249 (6)	0·4347 (3)	0·4378 (7)	0·4241 (4)	0·6929 (4)
N(2)	0·1368 (2)	−0·1890 (7)	0·4887 (4)	0·6083 (7)	0·3867 (4)	0·7214 (4)
N(3)	0·2305 (2)	−0·3002 (6)	0·5335 (4)	0·6411 (6)	0·2370 (3)	0·5348 (3)
N(4)	0·2570 (2)	−0·1452 (6)	0·4857 (4)	0·4634 (7)	0·2636 (4)	0·4907 (3)
N(5)	0·2867 (2)	0·2995 (7)	0·4320 (4)	0·0473 (7)	0·3237 (4)	0·4362 (3)
O(1)	0·1864 (2)	0·2984 (6)	0·3245 (3)	0·0870 (6)	0·4908 (3)	0·6348 (3)
O(2)*	0·25	0·66	0·25			
H(3)	0·068	−0·441	0·547	0·923 (7)	0·371 (4)	0·833 (4)
H(4)	0·032	−0·741	0·655	1·215 (9)	0·319 (5)	0·901 (5)
H(5)	0·095	−0·960	0·771	1·422 (12)	0·151 (6)	0·792 (5)
H(6)	0·196	−0·897	0·766	1·270 (9)	0·055 (5)	0·595 (4)
H(7)	0·232	−0·595	0·661	0·966 (8)	0·128 (4)	0·540 (4)
H(10)	0·111	0·532	0·221	−0·100 (8)	0·655 (5)	0·788 (4)
H(11)	0·011	0·459	0·225	0·047 (11)	0·758 (6)	0·977 (5)
H(12)	−0·026	0·156	0·331	0·352 (9)	0·699 (5)	1·045 (4)
H(13)	0·039	−0·082	0·431	0·549 (8)	0·543 (4)	0·910 (4)
H(15)	0·313	−0·326	0·662	0·278 (10)	0·044 (5)	0·382 (5)
H(16)	0·414	−0·378	0·673	0·173 (13)	−0·077 (7)	0·190 (6)
H(17)	0·474	−0·245	0·517	0·310 (8)	0·008 (5)	0·081 (4)
H(18)	0·432	−0·067	0·345	0·489 (11)	0·191 (6)	0·147 (5)
H(19)	0·331	−0·032	0·329	0·555 (10)	0·319 (5)	0·334 (5)
H(21)	0·282	0·443	0·463	−0·075 (9)	0·300 (5)	0·442 (5)
H(22)	0·326	0·311	0·468	0·073 (9)	0·269 (5)	0·381 (5)
H(23)	0·303	0·387	0·367	0·005 (11)	0·389 (6)	0·420 (5)

* Population parameter 0·3.

11·449 (2) Å, $\beta = 90·30$ (3)°, $V = 1809·3$ Å³, $Z = 4$, and $d_c = 1·45$ Mg m⁻³. The alternative space group Pn could be ruled out on the basis of the Patterson synthesis. 3229 independent reflections were measured on a Nonius CAD-4 automatic single-crystal diffractometer with graphite-monochromated Cu $K\alpha$ radiation. 441 of these had $I < 2\sigma(I)$ and were treated as unobserved. No absorption correction was applied ($\mu = 1·98$ mm⁻¹; crystal dimensions: 0·7 × 0·3 × 0·1 mm).

NIFORM

NIFORM was prepared by adding a solution of 2·6 g Ni^II nitrate hexahydrate in 10 ml water slowly to a warm solution of 2·4 g of the corresponding formazan in 700 ml methanol and 60 ml concentrated ammonia. This solution was refluxed for 0·5 h and cooled to room temperature, after which the complex was filtered off, washed with methanol and dried in vacuum over P_2O_5. Analysis: C 58·6 (58·50), H 4·36 (4·39), N 18·1 (17·96), O 4·33 (4·10), Ni 14·9% (15·5%) (in parentheses are the calculated percentages for $C_{19}H_{17}N_5NiO$).

Crystals of NIFORM are triclinic, space group $P\bar{1}$, with $a = 6·096$ (3), $b = 12·10$ (4), $c = 13·60$ (5) Å, $\alpha = 115·2$ (3), $\beta = 94·3$ (2), $\gamma = 93·4$ (3)°, $V = 900·7$ Å³, $Z = 2$, and $d_c = 1·45$ Mg m⁻³. The alternative space group $P1$ could be eliminated on the basis of the Patterson synthesis. 2769 independent reflections were collected as described for CUFORM; 740 of these had $I < 2\sigma(I)$ and were treated as unobserved. No absorption correction was applied ($\mu = 1·82$ mm⁻¹; crystal dimensions: 0·3 × 0·1 × 0·05 mm).

Structure determination and refinement

CUFORM

The coordinates of the Cu atom could be derived from a Patterson synthesis in terms of space group $P2/n$. From a Fourier synthesis based on Cu, all but one of the remaining non-hydrogen atoms could be located; the position of this atom was determined from geometrical considerations. After isotropic least-squares refinement a difference synthesis indicated all the H atoms. Further anisotropic refinement with weights $w = 1/(3·0 + F_o + 0·015F_o^2)$ and a dispersion correction for Cu converged to $R = 5·4\%$. The H atoms were kept fixed with isotropic temperature parameters equivalent to those of the carrier atoms. A final difference synthesis showed only one significant feature: a peak of height 2·5 e Å⁻³ at $y = 0·66$ along the twofold axis at $x = \frac{1}{4}$, $z = \frac{1}{4}$. Since the chemical analysis showed an excess of O, probably due to the occlusion of water by the crystal, the extra peak was

ascribed to O. Inserting 0·3 of an O atom at the above position resulted in a final R of 4·8% for .the 2788 observed reflections. The final parameters are listed in Table 1.*

NIFORM

An E^2 Patterson synthesis could be interpreted in terms of space group $P\bar{1}$ and yielded the positions of all non-hydrogen atoms. Isotropic least-squares refinement reduced R from 28 to 10%. Most of the H atoms were visible in a subsequent difference synthesis. Continued refinement, anisotropic for the non-hydrogen atoms and isotropic for H, in the course of which the missing H atoms were located, reduced R to 5·9%. A dispersion correction for Ni was included. The structure factors revealed discrepancies for a number of strong reflections in which systematically $|F_c| < |F_o|$.

* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33881 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
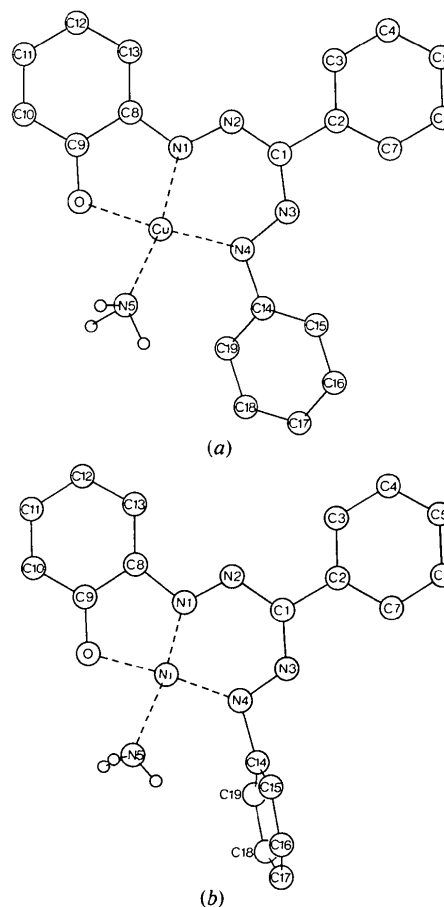

Fig. 1. Shape of the molecules: (a) CUFORM, (b) NIFORM.

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

	M = Cu	M = Ni		M = Cu	M = Ni
M—O	1·933 (4)	1·868 (7)	C(8)—N(1)	1·394 (7)	1·425 (9)
M—N(1)	1·930 (5)	1·840 (9)	C(9)—C(10)	1·403 (8)	1·399 (9)
M—N(4)	1·929 (4)	1·808 (7)	C(9)—O(1)	1·315 (7)	1·329 (9)
M—N(5)	1·998 (5)	1·939 (8)	C(10)—C(11)	1·385 (10)	1·373 (11)
C(1)—C(2)	1·486 (7)	1·466 (8)	C(11)—C(12)	1·363 (10)	1·403 (11)
C(1)—N(2)	1·348 (7)	1·388 (8)	C(12)—C(13)	1·393 (9)	1·375 (10)
C(1)—N(3)	1·338 (7)	1·333 (9)	C(14)—C(15)	1·376 (8)	1·370 (10)
C(2)—C(3)	1·418 (7)	1·398 (9)	C(14)—C(19)	1·397 (7)	1·372 (11)
C(2)—C(7)	1·378 (8)	1·383 (9)	C(14)—N(4)	1·439 (7)	1·444 (9)
C(3)—C(4)	1·397 (8)	1·381 (10)	C(15)—C(16)	1·392 (10)	1·374 (11)
C(4)—C(5)	1·358 (9)	1·353 (10)	C(16)—C(17)	1·370 (10)	1·368 (12)
C(5)—C(6)	1·407 (10)	1·382 (11)	C(17)—C(18)	1·393 (10)	1·374 (11)
C(6)—C(7)	1·388 (9)	1·385 (9)	C(18)—C(19)	1·392 (7)	1·379 (10)
C(8)—C(9)	1·416 (7)	1·377 (8)	N(1)—N(2)	1·294 (7)	1·257 (7)
C(8)—C(13)	1·396 (7)	1·414 (9)	N(3)—N(4)	1·318 (6)	1·321 (7)
O—M—N(1)	84·4 (2)	85·6 (3)	C(8)—C(9)—C(10)	117·5 (5)	119·1 (5)
O—M—N(4)	165·2 (2)	176·7 (2)	C(8)—C(9)—O(1)	119·7 (5)	118·6 (5)
O—M—N(5)	87·5 (2)	85·2 (3)	C(10)—C(9)—O(1)	122·7 (5)	122·3 (6)
N(1)—M—N(4)	89·4 (2)	92·3 (3)	C(9)—C(10)—C(11)	120·4 (6)	120·0 (6)
N(1)—M—N(5)	162·4 (2)	168·7 (2)	C(10)—C(11)—C(12)	120·9 (7)	120·8 (6)
N(4)—M—N(5)	102·0 (2)	97·2 (3)	C(11)—C(12)—C(13)	120·0 (7)	120·0 (5)
C(2)—C(1)—N(2)	115·3 (4)	114·8 (5)	C(8)—C(13)—C(12)	120·1 (6)	118·7 (6)
C(2)—C(1)—N(3)	114·6 (4)	117·3 (4)	C(15)—C(14)—C(19)	120·3 (5)	119·0 (5)
N(2)—C(1)—N(3)	130·1 (5)	127·9 (5)	C(15)—C(14)—N(4)	121·2 (5)	120·7 (6)
C(1)—C(2)—C(3)	119·9 (5)	121·2 (5)	C(19)—C(14)—N(4)	118·5 (4)	120·2 (5)
C(1)—C(2)—C(7)	121·9 (5)	121·1 (5)	C(14)—C(15)—C(16)	119·6 (6)	120·9 (7)
C(3)—C(2)—C(7)	118·2 (5)	117·6 (6)	C(15)—C(16)—C(17)	121·1 (7)	119·7 (7)
C(2)—C(3)—C(4)	118·8 (5)	120·5 (5)	C(16)—C(17)—C(18)	119·3 (7)	120·0 (6)
C(3)—C(4)—C(5)	122·2 (6)	121·4 (5)	C(17)—C(18)—C(19)	120·5 (6)	119·7 (7)
C(4)—C(5)—C(6)	119·6 (6)	119·1 (6)	C(14)—C(19)—C(18)	119·2 (5)	120·6 (6)
C(5)—C(6)—C(7)	118·5 (7)	120·4 (6)	C(8)—N(1)—N(2)	116·7 (5)	115·0 (5)
C(2)—C(7)—C(6)	122·7 (6)	120·9 (5)	C(1)—N(2)—N(1)	119·0 (5)	118·5 (5)
C(9)—C(8)—C(13)	121·0 (5)	121·3 (5)	C(1)—N(3)—N(4)	123·0 (5)	121·8 (4)
C(9)—C(8)—N(1)	112·0 (4)	110·5 (5)	C(14)—N(4)—N(3)	110·4 (4)	111·0 (4)
C(13)—C(8)—N(1)	127·0 (5)	128·1 (5)			

Therefore a few more cycles of refinement were run with an extinction parameter, g, included ($F_c^{corr} = F_c\{1 + g[(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)] F_c^2\}^{-1/4}$ (Larson, 1970). The final R was 4·7% for the 2029 observed reflections. The final g was $1·26 \times 10^{-5}$. A weighting function $w = 1/(5·2 + F_o + 0·017F_o^2)$ was applied. The final parameters are listed in Table 1.*

Results and discussion

The shapes of the molecules and the atomic numbering are given in Fig. 1. The bond distances and angles are listed in Table 2. The geometries of the coordination around Cu and Ni are depicted in Fig. 2. The bonds of Ni to its four coordinating atoms are systematically shorter (0·06–0·12 Å) than the corresponding bonds around Cu. The coordination around Ni is also considerably more planar than that around Cu. In both

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* See previous footnote.

molecules the three benzene rings are planar within the limits of accuracy, as is the formazan moiety N(1)N(2)C(1)N(3)N(4). Table 3 gives the angles between the three rings and the formazan moiety. It can be seen that the part C(1)–C(13), O, N(1)–N(4), Cu(Ni) is approximately planar (largest deviations from the best plane 0·11 and 0·09 Å respectively). The ring C(14)–C(19) is forced out of this plane by the presence of the NH_3 ligand, and is rotated by 30° in CUFORM, and by 80° in NIFORM because of the more compact coordination around Ni.
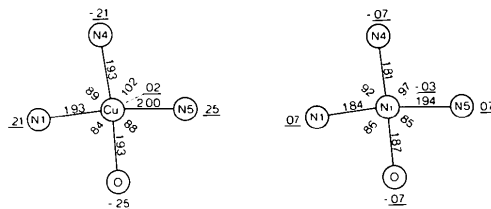

Fig. 2. Coordinations around the metal ions. The underlined numbers are the distances from the best plane through the four coordinating atoms.

Table 3. *Angles* (°) *between various planes*

Plane (I): C(2)–C(7)
Plane (II): C(8)–C(13),O
Plane (III): C(14)–C(19)
Plane (IV): N(1)N(2)C(1)N(3)N(4)

	CUFORM			NIFORM		
	(II)	(III)	(IV)	(II)	(III)	(IV)
(I)	3	29	6	5	79	2
(II)		31	4		84	3
(III)			32			80
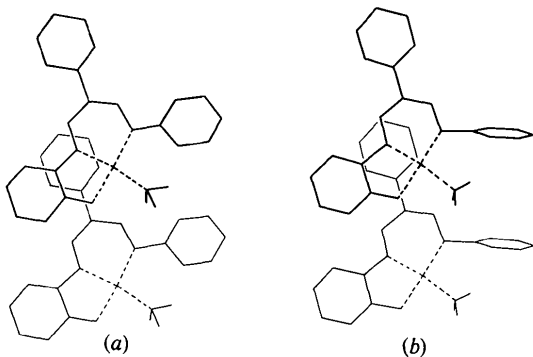
Fig. 3. Stacking of the molecules: (*a*) CUFORM, (*b*) NIFORM.

Fig. 4. Projections of (*a*) CUFORM along [010], and (*b*) NIFORM along [100]. The dashed line indicates the *B*-centred cell (see text).

Both structures consist of columns of similarly stacked molecules along the short axis. The stacking is depicted in Fig. 3. The two structures differ in the way the columns are packed; this is probably because of the difference in orientation of the phenyl groups C(14)–C(19).

The resemblance between the two structures is brought out by applying the transformation (0,1,2; 1,0,0; 0,1,0) to the basis vectors of NIFORM. This results in a *B*-centred cell with parameters: $a' = 24 \cdot 62$, $b' = 6 \cdot 10$, $c' = 12 \cdot 10$ Å, $\alpha' = 93 \cdot 4$, $\beta' = 88 \cdot 8$, $\gamma' = 96 \cdot 4°$. This should be compared with the cell parameters of CUFORM: $a = 24 \cdot 23$, $b = 6 \cdot 52$, $c = 11 \cdot 45$ Å, $\beta = 90 \cdot 3°$. In fact, the main difference between the two structures is that where CUFORM has an *n* glide NIFORM has a *B* translation. In Fig. 4 the projection along [010] of CUFORM is given together with the projection along [100] of NIFORM in which both the original and the transformed cell have been indicated. In both structures there are columns and inverted columns in equal numbers; only the arrangement of the columns is different: the diad axes in the cell of CUFORM have been replaced by inversion centres in NIFORM. In both structures the columns are connected in pairs by hydrogen bonds between N(5) and O of lengths 3·01 and 2·93 Å for CUFORM and NIFORM respectively (Fig. 4).

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