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Crystal and molecular structure of mono- and disubstituted [Ni(Bzo$_2$Me$_4$[14]hexaenatoN$_4$)] complexes. First X-ray characterization of the $-$C($=$NH)CN group

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Abstract

The macrocyclic complex [Ni(Bzo$_2$Me$_4$[14]hexaenatoN$_4$)] undergoes successive insertion by cyanogen at the two C–H methine groups. The primary reaction products do not show any ligand rearrangement and represent the first example of complexes bearing a cyanoiminomethyl substituent at a metallo-organic ring, for which the crystal and molecular structure has been determined by X-ray analysis. The mono- (**I**) and disubstituted complexes (**II**) crystallize in the orthorhombic *Pnca* (**I**) and monoclinic *C*2/*c* (**II**) space groups, with cell dimensions $a=22.354(3)$, $b=15.855(2)$, $c=11.417(2)$ Å ($Z=8$), and $a=21.813(3)$, $b=9.221(2)$, $c=11.185(2)$ Å, $\beta=99.1(2)°$ ($Z=4$), respectively. Their structures ($R_w=0.0386$ (**I**) and 0.0552 (**II**)) show a saddle-shaped deformation, which is enhanced by substitution of the methine hydrogen by the $-$C($=$NH)CN group. The structural parameters of this substituent show, *inter alia*, unusually high C$-$C($\equiv$N) (1.470(5) Å) and C–C(ring) (1.499(4) Å) bond distances, which well account for its observed thermal instability. In complex **II**, the two $=$NH hydrogen atoms interact with the two CN nitrogens of one faced molecule in an intermolecular hydrogen bond (H...N$=$2.64(5) Å, N–H...N$=$150(4)°).

Introduction

The reactivity of C–H acid compounds towards electrophiles in the presence of homogeneous metal catalysts has recently been the object of extensive investigations [1–5]. Most reactions involved β-dicarbonyls and nitriles or Michael acceptors to give metal-promoted C–C bond formation. The relevant metallo-organic catalytic intermediates has been isolated in a few cases and their structures determined. Rather surprisingly, no definite evidence was obtained until now of complexes deriving from 'simple' insertion of nitriles into the C–H methine group to give an α-type configuration, in which the resulting $-$C($=$NH)R substituent is bonded to the carbon atom in a α-position with respect to the metal-coordinated carbonyl groups. A ligand rearrangement was, in fact, generally observed to give a more stable linkage isomer, whose mode of metal–ligand coordination is presently under reinvestigation. It seemed therefore interesting to carry out an X-ray study on the solid state structure of the primary reaction products of cyanogen with the macrocyclic complex [Ni(C$_{22}$H$_{22}$N$_4$)], for which the rigid molecular structure should stabilize an α-configuration with uncoordinated cyanoiminomethyl groups (**I** and **II**).

No structural characterization has been reported until now on this particular atomic assembly in which one sp^2 C bears an $=$NH and a C$\equiv$N group.

Moreover, macrocyclic complexes based on the dibenzotetraaza[14]annulene framework are, in themselves, interesting because of their ability to mimic relevant aspects of biological systems [6–9] including some catalytic activity [10, 11]. Extensive work has been done in the synthesis [12–14] and

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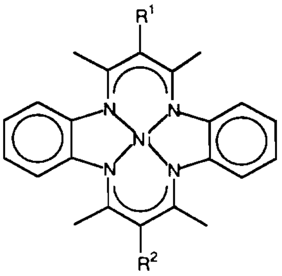


COMPOUNDS I,II

(I: R^1=H, R^2=-C(=NH)CN; II: R^1=R^2=-C(=NH)CN)

reactivity [15–18] of the dibenzotetraaza[14]annulene complexes and a number of them has been fully characterized by crystal structure determination [18–21]; no significant attention has been given, however, to how substitution on the macrocyclic ligand periphery affects the molecular structure.

Experimental

Synthesis of complexes

(2,3:9,10-Dibenzo-6-cyanoiminomethyl-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-k^4N)nickel(II), $[Ni(Bzo_2(C_2N_2H)Me_4[14]hexaenatoN_4)]$ (**I**) and (2,3:9,10-dibenzo-6,13-bis(cyanoiminomethyl)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-k^4N)nickel(II), $[Ni(Bzo_2(C_2N_2H)_2Me_4[14]hexaenatoN_4)]$ (**II**) were prepared as previously reported [18]. Crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane–hexane mixtures.

The intensities were collected on a Philips PW1100 four-circle diffractometer operating in the $\theta-2\theta$ scan mode (scan width 1.0°, scan speed 0.02° s^{-1}). During data collection, two standard reflections were measured every 180 min to check the stability of the crystal and the electronics. A summary of crystal and intensity collection data for complexes **I** and **II** is shown in Table 1.

The structures were solved using Multan80 and refined by full-matrix (complex **I**) or blocked-diagonal (complex **II**) least-squares methods, allowing all non-hydrogen atoms to vibrate anisotropically. The hydrogen atoms were located on a difference Fourier map and not refined except for the N–H imino hydrogen. All the calculations were carried out on a VAX 3400 computer with the SHELX 76 system of programs [22]. The residual R_w were 0.0386 (**I**)

TABLE 1. Summary of crystal and intensity collection data

Complex	I	II
Formula	$C_{24}H_{22}N_6Ni$	$C_{26}H_{22}N_8Ni$
M	453.21	505.25
Color	green–purple	green–purple
Habit	prismatic	prismatic
Crystal size (mm)	0.2×0.2×0.3	0.2×0.3×0.4
Crystal system	orthorhombic	monoclinic
Space group	*Pnca*	*C*2/*c*
a (Å)	22.354(3)	21.813(3)
b (Å)	15.855(2)	9.221(2)
c (Å)	11.417(2)	11.185(2)
β (°)		99.1(2)
V ($Å^3$)	4046.4	2221.4
Z	8	4
D_c (g cm^{-3})	1.488	1.511
λ (Å)	0.7107	0.7107
Temperature (°C)	21	21
Linear absorbance coefficient (cm^{-1})	8.36	7.68
Diffractometer	Philips PW1100	Philips PW1100
2θ Range (°)	$4 \leqslant 2\theta \leqslant 50$	$4 \leqslant 2\theta \leqslant 56$
Scan technique	θ–2θ	θ–2θ
Collected octants	*h*, *k*, *l*	*h*, *k*, *l*; −*h*, *k*, *l*
Total reflections collected	3573	2814
Unique reflections collected		2686 (*R*=0.0134)
Observed reflections ($F \geqslant 7\sigma(F)$)	2088	1714
Final residual *R*	0.0348	0.0489
Final residual R_w[a]	0.0386	0.0552

[a] $w=1/[\sigma^2(F)+0.00674F^2]$ (complex **I**) or $w=1/[\sigma^2(F)+0.00308F^2]$ (complex **II**).

and 0.0552 (**II**). The final fractional atomic coordinates for the non-hydrogen and the imino hydrogen atoms for I and II are listed in Tables 2 and 3 respectively.

Results and discussion

The macrocyclic complex [Ni(Bzo$_2$Me$_4$[14]hexaenatoN$_4$)] reacts with cyanogen to undergo insertion at the C–H methine group. The primary reaction products do not show any ligand rearrangement, so representing the first definite example of complexes bearing a $-$C(=NH)CN substituent at a metallo-organic ring. The mono- (**I**) and disubstituted complexes (**II**) crystallize in different systems, orthorhombic and monoclinic, and the crystal cell contains eight and four distinct molecules, respectively, with well defined intermolecular hydrogen bonds involving only complex **II** (see later). Both complexes adopt a saddle-shaped conformation, in which *o*-phenylene rings and diiminate chelate planes are tilted to opposite sites of the plane defined by the four nitrogen atoms. The distortion from planarity seems to be mainly due to steric interactions of the methyl substituents with the phenylene rings. This is consistent with the fact that the related unsubstituted [Ni(Bzo$_2$[14]hexaenatoN$_4$)] complex is almost flat [23]. Closer analysis of the structural parameters reveals definite, albeit small, differences in the molecular structures of complexes **I** and **II** (Figs. 1 and 2) and that of the related cyano derivative [Ni(Bzo$_2$(CN)Me$_4$[14]hexaenatoN$_4$)] (**III**) [18]. The discussion will be mainly based on the selected data of Table 4, with emphasis on the effect of the substituent at the methine carbon on bond lengths and saddle angles α, β, δ, ϵ, ω, as identified on Fig. 3 and Table 4.

TABLE 2. Fractional coordinates and thermal parameters for [Ni(Bzo$_2$(C$_2$N$_2$H)Me$_4$[14]hexaenatoN$_4$] (**I**)

Atom	*x*	*y*	*z*	$U_{iso/eq}$
Ni	0.21875(2)	0.11381(3)	0.24868(4)	0.0330(1)
N(1)	0.2193(1)	0.1225(2)	0.4116(3)	0.0380(9)
N(2)	0.1365(1)	0.0967(2)	0.2400(2)	0.036(1)
N(3)	0.2172(1)	0.1083(2)	0.0853(2)	0.036(1)
N(4)	0.3002(1)	0.1365(2)	0.2577(3)	0.0379(9)
N(5)	0.0457(2)	0.2755(2)	0.4867(3)	0.074(2)
N(6)	0.0323(2)	0.1173(3)	0.6782(4)	0.096(2)
C(1)	0.1737(2)	0.1511(2)	0.4748(3)	0.040(1)
C(2)	0.1160(2)	0.1621(2)	0.4241(3)	0.040(1)
C(3)	0.0974(2)	0.1298(2)	0.3151(3)	0.040(1)
C(4)	0.1219(2)	0.0538(2)	0.1347(3)	0.036(1)
C(5)	0.0737(2)	0.0000(3)	0.1169(3)	0.045(1)
C(6)	0.0668(2)	$-$0.0420(3)	0.0123(4)	0.050(1)
C(7)	0.1088(2)	$-$0.0310(3)	$-$0.0767(4)	0.054(2)
C(8)	0.1585(2)	0.0203(3)	$-$0.0583(3)	0.048(1)
C(9)	0.1662(2)	0.0622(2)	0.0470(3)	0.038(1)
C(10)	0.2561(2)	0.1481(2)	0.0167(3)	0.040(1)
C(11)	0.3078(2)	0.1850(2)	0.0609(3)	0.043(1)
C(12)	0.3308(2)	0.1766(2)	0.1744(3)	0.042(1)
C(13)	0.3225(2)	0.1144(2)	0.3691(3)	0.040(1)
C(14)	0.3813(2)	0.0924(3)	0.3950(4)	0.050(2)
C(15)	0.3960(2)	0.0642(3)	0.5057(5)	0.063(2)
C(16)	0.3527(2)	0.0578(3)	0.5921(4)	0.061(2)
C(17)	0.2936(2)	0.0787(3)	0.5664(3)	0.051(1)
C(18)	0.2781(2)	0.1071(2)	0.4562(3)	0.040(1)
C(19)	0.1814(2)	0.1791(3)	0.6004(3)	0.051(2)
C(20)	0.0311(2)	0.1341(3)	0.2819(4)	0.055(2)
C(21)	0.2446(2)	0.1609(3)	$-$0.1127(4)	0.056(2)
C(22)	0.3896(2)	0.2196(3)	0.1985(4)	0.060(2)
C(23)	0.0696(2)	0.2041(3)	0.4995(4)	0.050(1)
C(24)	0.0481(2)	0.1561(3)	0.6008(4)	0.061(2)
H(1)	0.060(2)	0.302(3)	0.424(4)	

TABLE 3. Fractional coordinates and thermal parameters for [Ni(Bzo$_2$(C$_2$N$_2$H)$_2$Me$_4$[14]hexaenatoN$_4$] (**II**)

Atom	*x*	*y*	*z*	$U_{iso/eq}$
Ni	1.000000	0.24385(8)	0.250000	0.0265(2)
N(2)	0.9148(1)	0.2474(3)	0.1987(3)	0.0285(8)
N(3)	1.0073(1)	0.2412(3)	0.0880(3)	0.0290(9)
N(5)	0.8154(2)	$-$0.0519(5)	0.4104(4)	0.054(1)
N(6)	0.8055(2)	0.1951(7)	0.6234(4)	0.080(2)
C(1)	0.9467(2)	0.1780(4)	0.4563(3)	0.031(1)
C(2)	0.8897(2)	0.1461(4)	0.3813(3)	0.032(1)
C(3)	0.8725(2)	0.1931(4)	0.2595(3)	0.031(1)
C(4)	0.9026(2)	0.3115(4)	0.0807(3)	0.031(1)
C(5)	0.8506(2)	0.3905(5)	0.0300(4)	0.042(1)
C(6)	0.8474(2)	0.4543(5)	$-$0.0834(4)	0.053(2)
C(7)	0.8972(2)	0.4386(5)	$-$0.1464(4)	0.049(2)
C(8)	0.9509(2)	0.3672(5)	$-$0.0945(4)	0.042(1)
C(9)	0.9538(2)	0.3028(4)	0.0180(3)	0.031(1)
C(19)	0.9560(2)	0.1266(5)	0.5872(4)	0.042(1)
C(20)	0.8051(2)	0.1850(5)	0.2026(4)	0.043(1)
C(23)	0.8417(2)	0.0680(5)	0.4388(4)	0.040(1)
C(24)	0.8200(2)	0.1408(6)	0.5415(4)	0.050(2)
H(1)	0.829(2)	$-$0.083(5)	0.343(4)	

Bond distances and angles

Complexes **I** and **II** adopt a square-planar configuration, in which the metal centre is surrounded by the four nitrogen atoms. In the case of complex **I** the nickel atom is slightly displaced out of the {NNNN} plane (0.036(1) Å) in the opposite direction of the two benzene moieties. No significant differences are observed in the Ni–nitrogen distances (1.850(2)–1.862(2) Å), which seem to be scarcely affected by substitution at the methine carbon of the metallo-organic ring and are closely related to those of the parent unsubstituted [Ni(C$_{22}$H$_{22}$N$_4$)] (**IV**) complex (1.866(3) Å) [20]. The N–C distances of the macrocyclic ligand lie also within the expected

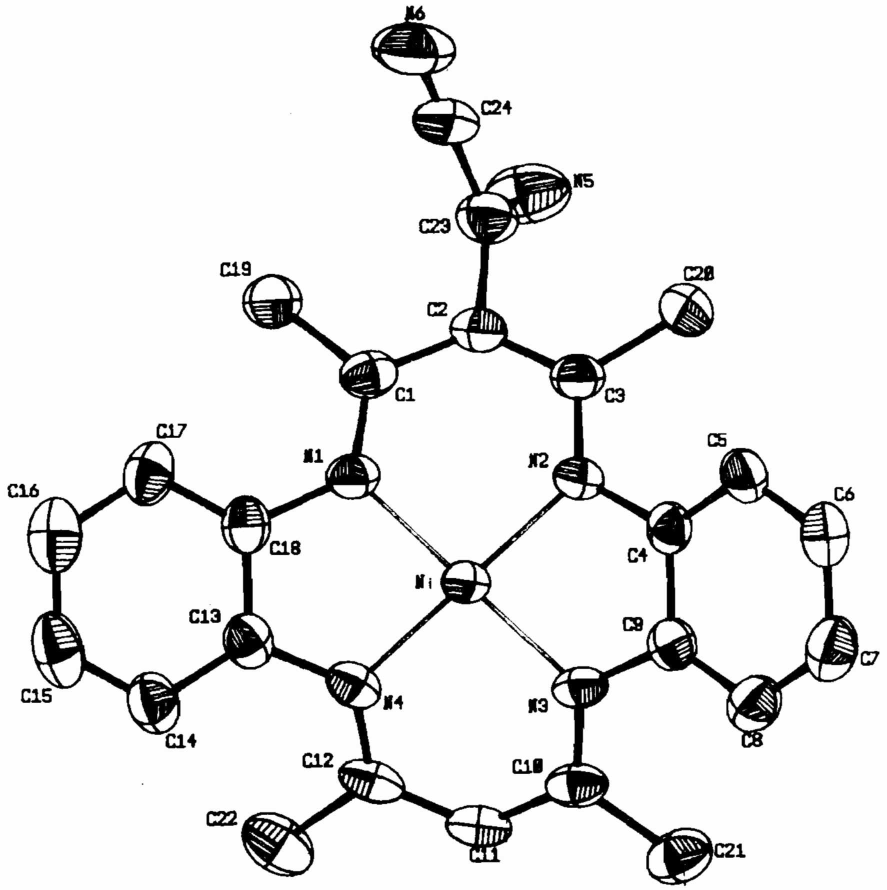


Fig. 1. ORTEP view of [Ni(Bzo$_2$(C$_2$N$_2$H)Me$_4$[14]hexaenatoN$_4$)] (I).

range (1.325(4)–1.332(4) Å) of values, which are between those characteristic of N–C(sp^2) (1.36 Å) and N=C (1.28 Å) bonds [24]. However, a definite, albeit small, effect of substitution at the C$_2$ atom is observed for the C$_2$–C$_1$/C$_3$ bond lengths; in fact, the values of 1.417(4) (**I**) and 1.420(4) (**II**) Å are slightly over those of the corresponding C$_2$'–C$_1$'/C$_3$' bonds. Noticeably, these last distances are very similar in **I** (1.395(4) Å), **III** (1.394(11) Å), and in the unsubstituted complex **IV** (1.393(3) Å) [20], so indicating a negligible effect of substitution on the opposite half of the macrocycle. Since the typical sp^2–sp^2 carbon–carbon distances are 1.48 and 1.34 Å for a single and a double bond, respectively, it is clearly seen that the bond order 1.5 is slightly reduced by the substitution at the carbon C$_2$. A similar effect was already observed in the C$_1$/C$_3$ positions; in fact the prototype complex [Ni(Bzo$_2$[14]hexaenatoN$_4$)] exhibit even smaller C$_2$–C$_1$/C$_3$ distances (1.383(2) Å) [23] with respect to the tetramethyl-substituted complex **IV**. Structural parameters of the substituent –C(=NH)CN group (see also later) reveal unusually high values of the C$_2$–C bond length (1.503(5) (**I**) and 1.496(6) (**II**) Å), which are usually considered as typical for sp^3–sp^2 carbon–carbon bonds [24, 25]. The other bond distances and, in general, bond angles (Tables 5 and 6) seem not to require particular comments.

Saddle angles

As already pointed out, there is a saddle-shaped deformation of the macrocycle (Figs. 3 and 4) mainly because of the mutual repulsion of the methyl and phenyl groups. Substitution at the methine carbon further enhances this deformation. The dihedral angle increases, for example, from 24.2 (α') to 26.6° (α) in complex **I** and similar behaviour was observed for **III** (21.9–26.9°). This substitution plays a specific role also in the deviation of the {C$_1$C$_2$C$_3$} from the {NNC$_1$C$_3$} plane, as measured by β which changes from 7.2 to 10.6° (**I**). This last value is close to that found for the disubstituted complex **II** (9.8°) and can be compared with the smaller value (5.2°) exhibited by the cyano derivative **III**. On the whole, substitution of the methine H by one –C(=NH)CN group produces the fairly large deviation of the

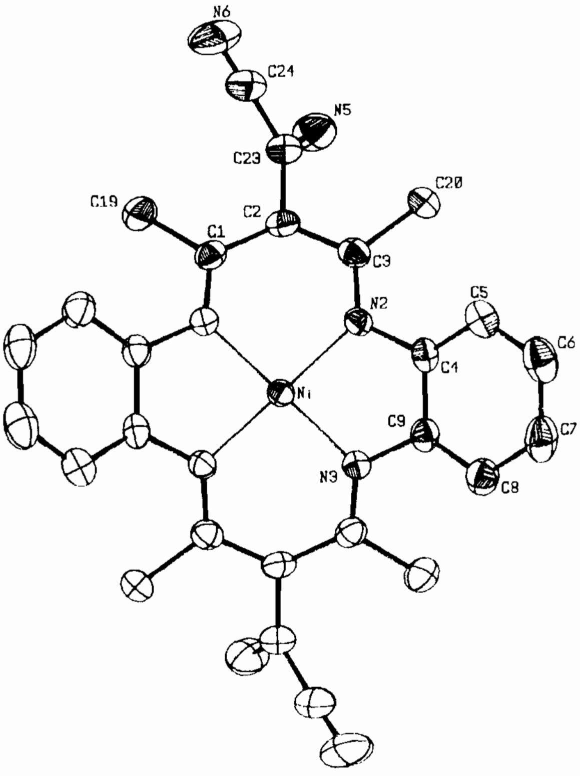


Fig. 2. ORTEP view of [Ni(Bzo$_2$(C$_2$N$_2$H)$_2$Me$_4$[14]-hexaenatoN$_4$)] (**II**).

{C$_1$C$_2$C$_3$} from the {NNNN} plane of 37.2 instead of 31.4°. The aryl groups behave differently in **I** and **II**; in the first case the dihedral angle ω is only slightly larger than that found in the unsubstituted complex **IV** (29.0 versus 27.4°) [20], whereas the presence of two $-$C(=NH)CN substituents in **II** has a great effect on the saddle angle ω, which takes a value of 32.6°. Inspection of the data reveals that this is mainly resulting from a distortion of the {NC$\overset{\dots}{-}$CN} plane; in fact, the dihedral angle ϵ has a value of 26.3° considerably higher than those found in the monosubstituted complexes **I** and **III** (22.9 and 22.4°).

The $-C(=NH)CN$ group

The central carbon atom adopts a planar geometry, with an sp^2 hybridization clearly away from the ideal. The structural parameters show characteristic and rather unusual features. In general, it is seen that the carbon–carbon bonds are rather lengthened; in fact, the mean C$-$C($\equiv$N) bond distance for complexes **I** and **II** is 1.470(5) Å, which appears over the expected value for a sp^2–sp carbon bond (1.42–1.43 Å) [24, 25] and is higher, for example, than that found in the similar cyano complex **III** (1.444(14) Å). The reason for this cannot be at-

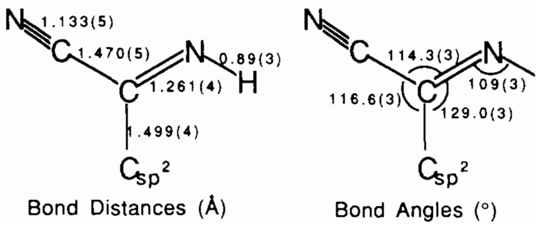


TABLE 4. Structural parameters for complexes **I**–**III**[a]

	I	II	III[b]
Bond distances (Å)			
Ni–N	1.862	1.850	1.852
Ni–N′	1.861	1.850	1.868
N–C$_1$/C$_3$	1.330	1.325	1.334
N–C$_1$′/C$_3$′	1.332	1.325	1.340
C$_2$–C$_1$/C$_3$	1.417	1.420	1.408
C$_2$′–C$_1$′/C$_3$′	1.395	1.420	1.394
N–C(Ph)	1.425	1.424	1.421
N′–C(Ph)	1.417	1.424	1.416
C$-$C(=NH)	1.503	1.496	
C$-$C($\equiv$N)	1.466	1.473	1.444
C=N(H)	1.260	1.263	
C$\equiv$N	1.134	1.132	1.141
N–H	0.888	0.899	
Dihedral angles (°)			
α	26.6	24.3	26.9
α'	24.2	24.3	21.9
β	10.6	9.8	5.2
β'	7.2	9.8	3.5
ϵ	22.9	26.3	22.4
ω	29.0	32.6	27.9
δ	75.6	61.9	

[a] Mean values when appropriate: individual standard deviations of the distances for non-hydrogen atoms <0.007 (complexes **I** and **II**) of <0.015 Å (complex **III**); standard deviations for dihedral angles <0.4 (complexes **I** and **II**) or <1.0° (complex **III**); atom labels and keys to α, α', β, β' and δ are in Fig. 3; ϵ and ω are angles of the {NNNN} plane with the {NC$\overset{\dots}{-}$CN} and {aryl} planes, respectively (see, for a better understanding, Figs. 1 and 2); absolute values of the angles are reported (diiminato and aryl planes are tilted in opposite directions). [b] From ref. 18.

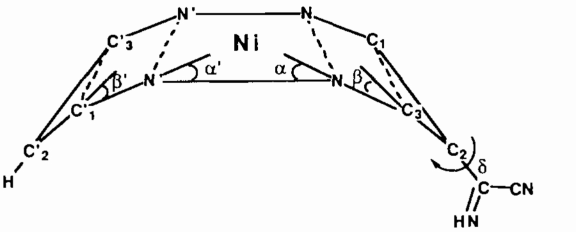


Fig. 3. α = Dihedral angle between {NNNN} and {NNC$_1$C$_3$} planes; β = dihedral angle between {NNC$_1$C$_3$} and {C$_1$C$_2$C$_3$} planes; δ = dihedral angle between {NNNN} and {C$_2-$C(=NH)CN} planes; aryl groups are omitted. Substituents at the methine carbon are relative to complex **I**; complex **II** has two C(=NH)CN substituents and complex **III** one CN.

TABLE 5. Selected bond distances (Å) and angles (°) for [Ni(Bzo$_2$(C$_2$N$_2$H)Me$_4$[14]hexaenatoN$_4$] (**I**)

Ni–N(1)	1.865(3)	Ni–N(2)	1.860(3)
Ni–N(3)	1.868(3)	Ni–N(4)	1.858(3)
N(1)–C(1)	1.329(5)	N(1)–C(18)	1.431(5)
N(2)–C(3)	1.332(5)	N(2)–C(4)	1.420(4)
N(3)–C(9)	1.423(5)	N(3)–C(10)	1.331(5)
N(4)–C(12)	1.333(5)	N(4)–C(13)	1.411(5)
N(5)–C(23)	1.260(6)	N(6)–C(24)	1.134(6)
C(1)–C(2)	1.424(5)	C(1)–C(19)	1.511(5)
C(2)–C(3)	1.410(5)	C(2)–C(23)	1.503(5)
C(3)–C(20)	1.531(5)	C(4)–C(5)	1.388(5)
C(4)–C(9)	1.414(5)	C(5)–C(6)	1.376(6)
C(6)–C(7)	1.394(6)	C(7)–C(8)	1.393(6)
C(8)–C(9)	1.385(5)	C(10)–C(11)	1.391(5)
C(10)–C(21)	1.513(5)	C(11)–C(12)	1.400(5)
C(12)–C(22)	1.505(6)	C(13)–C(14)	1.390(5)
C(13)–C(18)	1.410(5)	C(14)–C(15)	1.380(6)
C(15)–C(16)	1.386(7)	C(16)–C(17)	1.394(6)
C(17)–C(18)	1.381(6)	C(23)–C(24)	1.466(6)
N(3)–Ni–N(4)	94.8(1)	N(2)–Ni–N(4)	177.2(1)
N(2)–Ni–N(3)	85.5(1)	N(1)–Ni–N(4)	85.7(1)
N(1)–Ni–N(3)	178.3(1)	N(1)–Ni–N(2)	94.0(1)
Ni–N(1)–C(18)	110.4(2)	Ni–N(1)–C(1)	124.2(2)
C(1)–N(1)–C(18)	124.7(3)	Ni–N(2)–C(4)	110.1(2)
Ni–N(2)–C(3)	123.9(2)	C(3)–N(2)–C(4)	125.5(3)
Ni–N(3)–C(10)	123.6(2)	Ni–N(3)–C(9)	110.2(2)
C(9)–N(3)–C(10)	126.0(3)	Ni–N(4)–C(13)	110.4(2)
Ni–N(4)–C(12)	123.8(3)	C(12)–N(4)–C(13)	125.4(3)
N(1)–C(1)–C(19)	121.9(3)	N(1)–C(1)–C(2)	121.0(3)
C(2)–C(1)–C(19)	117.0(3)	C(1)–C(2)–C(23)	116.5(3)
C(1)–C(2)–C(3)	125.6(3)	C(3)–C(2)–C(23)	117.5(3)
N(2)–C(3)–C(2)	121.1(3)	C(2)–C(3)–C(20)	119.2(3)
N(2)–C(3)–C(20)	119.6(3)	N(2)–C(4)–C(9)	113.1(3)
N(2)–C(4)–C(5)	126.7(3)	C(5)–C(4)–C(9)	119.9(3)
C(4)–C(5)–C(6)	120.7(3)	C(5)–C(6)–C(7)	119.8(4)
C(6)–C(7)–C(8)	120.0(4)	C(7)–C(8)–C(9)	120.6(4)
C(4)–C(9)–C(8)	118.8(3)	N(3)–C(9)–C(8)	127.7(3)
N(3)–C(9)–C(4)	113.1(3)	N(3)–C(10)–C(21)	121.8(3)
N(3)–C(10)–C(11)	122.0(3)	C(11)–C(10)–C(21)	116.1(3)
C(10)–C(11)–C(12)	126.9(3)	N(4)–C(12)–C(11)	121.1(3)
C(11)–C(12)–C(22)	116.5(3)	N(4)–C(12)–C(22)	122.3(4)
N(4)–C(13)–C(18)	114.0(3)	N(4)–C(13)–C(14)	126.0(3)
C(14)–C(13)–C(18)	119.6(3)	C(13)–C(14)–C(15)	120.1(4)
C(14)–C(15)–C(16)	120.6(4)	C(15)–C(16)–C(17)	119.6(4)
C(16)–C(17)–C(18)	120.5(4)	C(13)–C(18)–(17)	119.5(3)
N(1)–C(18)–C(17)	127.6(3)	N(1)–C(18)–C(13)	112.5(3)
N(5)–C(23)–C(2)	128.7(4)	C(2)–C(23)–C(24)	116.5(4)
N(5)–C(23)–C(24)	114.7(4)	N(6)–C(24)–C(23)	178.3(5)

TABLE 6. Selected bond distances (Å) and angles (°) for [Ni(Bzo$_2$(C$_2$N$_2$H)$_2$Me$_4$[14]hexaenatoN$_4$] (**II**)

Ni–N(2)	1.856(3)	Ni–N(3)	1.844(3)
N(2)–C(3)	1.329(5)	N(2)–C(4)	1.432(5)
N(3)–C(9)	1.417(5)	N(5)–C(23)	1.263(6)
N(6)–C(24)	1.132(7)	C(1)–C(2)	1.418(6)
C(1)–C(19)	1.522(6)	C(2)–C(3)	1.422(5)
C(2)–C(23)	1.496(6)	C(3)–C(20)	1.508(6)
C(4)–C(5)	1.392(6)	C(4)–C(9)	1.411(6)
C(5)–C(6)	1.390(7)	C(6)–C(7)	1.391(8)
C(7)–C(8)	1.390(6)	C(8)–C(9)	1.384(6)
C(23)–C(24)	1.473(7)		
N(2)–Ni–N(3)	86.2(3)	Ni–N(2)–C(4)	108.9(5)
Ni–N(2)–C(3)	125.3(3)	C(3)–N(2)–C(4)	125.8(7)
Ni–N(3)–C(9)	110.3(3)	C(2)–C(1)–C(19)	118.4(5)
C(1)–C(2)–C(23)	117.0(4)	C(1)–C(2)–C(3)	125.3(5)
C(3)–C(2)–C(23)	117.5(5)	N(2)–C(3)–C(2)	120.4(7)
C(2)–C(3)–C(20)	118.7(5)	N(2)–C(3)–C(20)	120.8(4)
N(2)–C(4)–C(9)	112.8(5)	N(2)–C(4)–C(5)	127.7(5)
C(5)–C(4)–C(9)	119.1(4)	C(4)–C(5)–C(6)	120.8(7)
C(5)–C(6)–C(7)	119.3(6)	C(6)–C(7)–C(8)	120.8(5)
C(7)–C(8)–C(9)	119.8(7)	C(4)–C(9)–C(8)	120.1(6)
N(3)–C(9)–C(8)	126.1(7)	N(3)–C(9)–C(4)	113.3(4)
N(5)–C(23)–C(2)	129.3(4)	C(2)–C(23)–C(24)	116.7(4)
N(5)–C(23)–C(24)	113.9(5)	N(6)–C(24)–C(23)	177.1(7)

tributed to steric interactions with the macrocyclic ring or the metal centre, so that, this behaviour seems to represent an intrinsic property of this peculiar atomic assembly. Also the C–C$_2$ bond is, as mentioned above, rather long, but we cannot rule out that in this case steric repulsion plays some role. In fact, the H atom is forced rather close to the C$_2$ carbon (interatomic distance = 2.52(4) Å) and this negative interaction may be responsible, at least in part, for the observed lengthening of the C–C$_2$ bond and for the fairly large C$_2$–C=NH angle (129.0(3)°). The double C=N(H) (1.261(4) Å) and triple C≡N (1.133(5) Å) bonds are less sensitive to the nature of the surrounding atoms and the values of their distances fall in the range characteristic of imino [26] and cyano [18, 27] groups. The position of the hydrogen atom, which has been easily located on a difference Fourier map, assumes the correct distance from the imino nitrogen and is scarcely affected by the occurrence of an intermolecular hydrogen bond in **II**. Figure 4 shows how the two imino hydrogen atoms nicely interact with the two cyano nitrogens of one faced molecule ((N=)H...N(≡C) = 2.64(5) Å; N–H...N = 150(4)°). An overall picture of the macrocycle and of the cyanoiminomethyl substituent shows that the C$_2$C(=NH)CN plane is twisted away substantially from the {NNNN} plane (δ = 75.6 (**I**) and 61.9° (**II**)). The high δ values observed indicate that the substituent adopts the orientation in which interactions between the =NH hydrogen, the C$_2$ carbon and the CH$_3$ group are minimal.

The whole of these data can be compared with those found on a series of related Jäger complexes [28]. In that case the C$_2$/C$_1$–C$_3$ distances were in the range 1.435(3)–1.417(2) Å (n = 3; R = CCl$_3$ and CH$_3$, respectively (Fig. 5)), similar to that found in complexes **I** and **II**. This similarity extends to the dihedral angle β, which showed values around 10° in correspondence with the shorter C$_2$/C$_1$–C$_3$ distances. The situation is markedly different for the C$_2$–C(substituent) bond; in fact, the bond lengths were much shorter (1.419(3)–1.469(2) Å versus

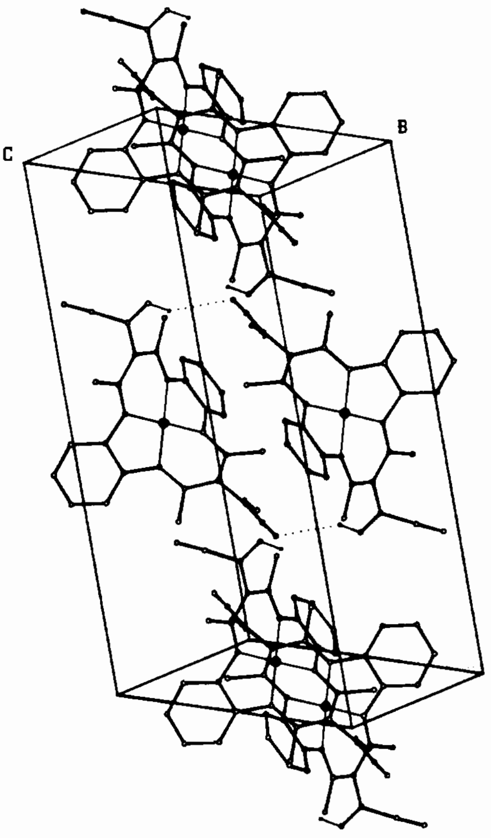
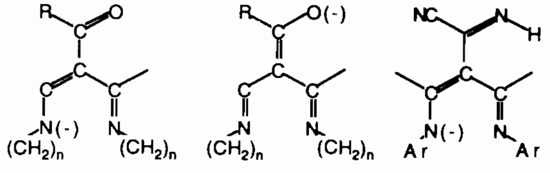


Fig. 4. Packing diagram of [Ni(Bzo$_2$(C$_2$N$_2$H)$_2$Me$_4$[14]-hexaenatoN$_4$)] (**II**) in the unit cell. Dotted lines represent intermolecular hydrogen bonds; (N=)H...N(≡C)=2.64(5) Å; N−H...N=150(4)°.



(a) (b) (c)

Fig. 5. Prevalent canonical forms for Jäger [28] complexes (a, b) and complexes **I** and **II** (c). Double bonds in the 1,3-diiminato ring are interchangeable.

1.499(4) Å) and the torsion angle of the substituent δ much smaller (22.2–6.4° versus 75.6 (**I**) or 61.9° (**II**)). This allows us to conclude that the canonical form (b), in which a double bond extends from the macrocycle to the substituent, plays as noticed an important role in the reported Jäger complexes [28], but a negligible one in **I** and **II**, which are well represented by form (c). This last consideration and, in general, all the structural parameters well justify the apparent instability of the −C(=NH)CN group towards dissociation from the macrocycle or towards release of HCN [18], both processes involving rupture of unusually long single C–C bonds.

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