Template Synthesis, Structure and Properties of a Bis(macrocyclic) Dinickel(II) Complex based on a 14-Membered Hexaaza Unit‡

Vladimir B. Arion,*,†,[a] **Nicolai V. Gerbeleu,**[a] **Veaceslav G. Levitsky,**[a] **Yuri A. Simonov,**[b] **Alexandr A. Dvorkin**[b] **and Polina N. Bourosh**[b]

[a] *Institute of Chemistry of the Moldova Academy of Sciences, Academy Street 3, 277028 Kishinev, Moldova*

[b] *Institute of Applied Physics of the Moldova Academy of Sciences, Academy Street 5, 277028 Kishinev, Moldova*

Template condensation of $[Ni_2L^2]$ $\{H_6L^2$ = tetrakis[1-(3-methylisothiosemicarbazono)ethyl]ethane$\}$ with 3-ethoxyacrylaldehyde in dimethylformamide resulted in a new type of dinickel(II) bis(macrocyclic) complex, in which two hexaazamacrocyclic subunits are linked by a single C–C bond. The complex was characterized by means of spectral analysis (UV/VIS, ^{1}H NMR, electron-impact mass), magnetic susceptibility measurements and X-ray analysis. Peculiarities of the crystal structure in comparison to related mono- and bi-nuclear species were revealed.

The formation and investigation of molecules containing spatially separated and sterically well defined reactive sites continues to be one of the most attractive and active areas of co-ordination chemistry. In particular polyazamacrocyclic binuclear complexes containing two similar or two dissimilar metal ions are becoming increasingly important in the modelling of active sites in biological systems[1–3] and in the study of metal–metal electronic and magnetic interactions.[4–8] They exhibit catalytic properties[9–11] often better than those of the corresponding mononuclear species. This is due to the high thermodynamic stability and kinetic non-lability, the ability to change oxidation states and the presence in the co-ordination sphere of the metal ion of one or two positions accessible for binding of additional ligands.

In this paper we report the synthesis of a new ditopic nickel(II) complex and a detailed study of its structure and spectral properties in comparison with monocyclic hexaaza and open-chain precursors.

Experimental

The complex $[Ni_2L^2]$ $\{H_6L^2$ = tetrakis[1-(3-methylisothiosemicarbazono)ethyl]ethane$\}$ was prepared by reaction of $[Ni(H_2L^1)]I{\cdot}0.5MeOH$[12] $\{H_3L^1$ = bis[1-(3- methylisothiosemicarbazono)ethyl]methane$\}$ and aqueous ammonia in methanol.[13] 3-Ethoxyacrylaldehyde was prepared by hydrolysis of 1,1,3,3-tetraethoxypropane in slightly acidic solution.[14]

Synthesis of $[Ni_2L^3]$.—A mixture of $[Ni_2L^2]$ (0.39 g, 0.06 mmol) and 3-ethoxyacrylaldehyde (1 cm^3) in dimethylformamide (dmf) (30 cm^3) was heated to 100 °C for 4 h. The deep green solution became light brown. The solvent was evaporated to dryness under reduced pressure, the residue dissolved in chloroform and the product precipitated by addition of ethanol. The crude product was purified by column chromatography on silica, using chloroform as eluent. Yield 0.17 g, 39.5% (Found: C, 40.05; H, 4.2; N, 22.7. Calc. for $C_{24}H_{30}N_{12}Ni_2S_4$: C, 39.45; H, 4.1; N, 23.0%.) ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.06 (4 H, d, J = 6.4, CH=N), 5.11 (2 H, t, J = 6.4 Hz, =CH), 2.46 (12 H, s, SCH_3) and 2.08 (12 H, s, CH_3). Single crystals of $[Ni_2L^3]$ of sufficient quality for X-ray analysis were grown from saturated chloroform–hexane solution at room temperature.

The C, H, N contents were determined by standard micromethods. Electron-impact mass spectra were measured on a MX-1320 double-focusing mass spectrometer (PO 'Nauchpribor', Orel, Russia) using a direct-inlet system at 200–260 °C, a temperature of the ionization chamber 60–70 °C higher than the evaporation temperature, an emission current of 10 mA, and an ionization energy of 70 eV (*ca.* 1.12×10^{-17} J). Magnetic susceptibilites were measured on a Gouy balance. The ^{1}H NMR spectrum was recorded on a Bruker WP-80 spectrometer in $CDCl_3$ with $SiMe_4$ as an internal standard, electronic spectra using a Specord UV/VIS spectrophotometer.

Crystallography.—A suitable brown prism of $[Ni_2L^3]$, dimensions 0.2 × 0.2 × 0.7 mm, was placed in an RED-4 diffractometer (Mo-Kα radiation, θ–2θ scan technique) to collect reflection data. In order to develop and refine the crystal structure, 2384 reflections satisfying $I \geqslant 3\sigma(I)$ were used; the dependent reflections were averaged. Corrections were applied for Lorentz and polarization factors when converting from intensities to structure factors, but not for absorption. The structure was solved by the heavy-atom technique using the SHELX 76 program.[15] The non-hydrogen atoms found from Fourier syntheses were refined anisotropically and the H atoms isotropically. The final R factor was 0.0742. The crystallographic data, atomic coordinates, interatomic distances and bond angles are presented in Tables 1–3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

A simple and efficient route to build up bis(macrocyclic) structures is shown in Scheme 1. In the first step $[Ni(H_2L^1)]I$ is obtained in good yield starting from the corresponding building blocks in the presence of the nickel(II) salt in methanol

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† *Present address:* Max-Planck-Institut für Kohlenforschung, 45466 Mülheim an der Ruhr, Germany.

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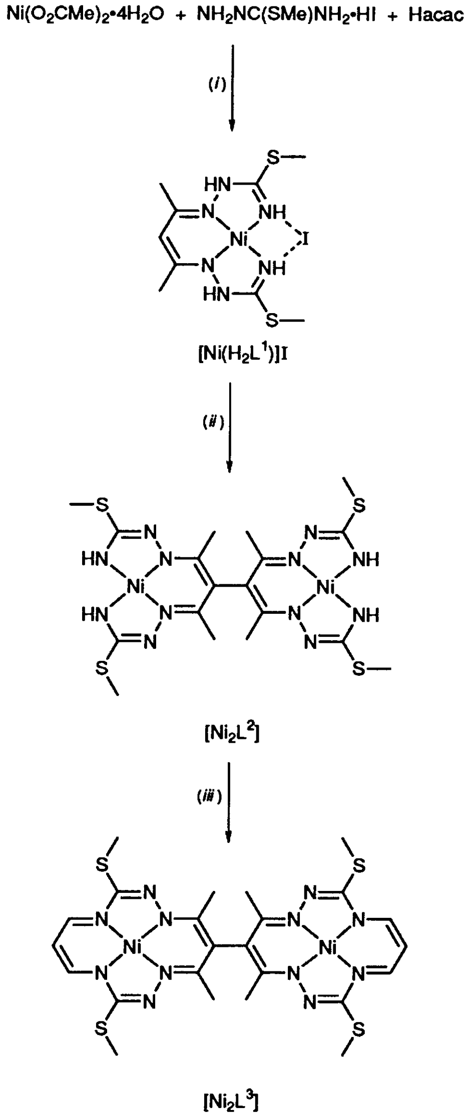

Scheme 1 acac = Acetylacetonate. (*i*) MeOH, 60 °C; (*ii*) NH_4OH, I_2, MeOH; (*iii*) 3-ethoxyacrylaldehyde, dmf, 100 °C, 4 h

solution.[12] By deprotonation and oxidative coupling involving γ-carbon atoms, it is easily converted to the dimeric species $[Ni_2L^2]$ in nearly quantitative yield. Finally, heating of $[Ni_2L^2]$ with 3-ethoxyacrylaldehyde in dmf leads to the binuclear macrocyclic complex $[Ni_2L^3]$ in 40% yield. The light brown crystals of $[Ni_2L^3]$ are soluble in chloroform and benzene, but insoluble in hexane, light petroleum, ethanol and water.

The product $[Ni_2L^3]$ is diamagnetic. Data from EI mass spectral analysis are consistent with the proposed structure. A peak at *m*/*z* 730, corresponding to the parent ion $[M]^+$, was the most intense. It should be noted that the C–C bond connecting the two halves of the dimeric unit is more stable to EI than that in the starting material $[Ni_2L^2]$. The molecular peak for the latter was not observed in the EI mass spectrum. The most intense peak occurred at *m*/*z* 329, corresponding to one half of the molecule.

The crystal structure of the complex $[Ni_2L^3]$ is consistent with a binuclear species as shown in Fig. 1. The structure is molecular. There are only van der Waals interactions between the molecules. It should be noted that the crystal structure of the precursor contains two symmetry-independent binuclear complex molecules (A and B). These are associated as two pairs A,A* and B,B* through a Ni••• Ni interaction.[13] No tendency to form a stacked structure by interaction between cyclic fragments of binuclear molecules, as well as additional weak Ni•••L^3 or Ni•••Ni interactions between neighbouring molecules of $[Ni_2L^3]$ was observed.

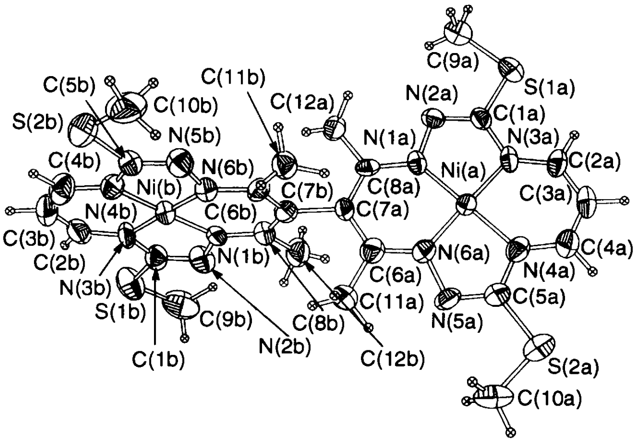

Fig. 1 Molecular structure of $[Ni_2L^3]$, showing the thermal vibration ellipsoids (at the 50% probability level) and the atom-numbering scheme

Table 1 Crystallographic data for $[Ni_2L^3]$

Formula	$C_{24}H_{30}N_{12}Ni_2S_4$
M	732.20
System	Monoclinic
Space group	$P2_1/n$
a/Å	18.366(4)
b/Å	18.221(5)
c/Å	9.198(4)
β/°	90.20(2)
U/Å^3	3078(3)
Z	4
T/°C	20 ± 1
λ(Mo-Kα)/Å	0.710 69
D_c/g cm^{-3}	1.599(3)
μ/cm^{-1}	15.20
F(000)	1496
h,*k*,*l* ranges	0–20, 0–19, −10 to 10
θ_{max}/°	23
R	0.074 (*w* = 1)

Square-planar co-ordination around the nickel ions is evident in both crystallographically independent halves of the binuclear structure. The mean Ni–N(1) and Ni–N(3) distances are 1.79 and 1.82 Å, respectively. They are shorter than in the related open-chain precursor $[Ni_2L^2]$[13] (1.848 and 1.836 Å), mononuclear $[Ni(H_2L^1)]I$[12] (1.851 and 1.831 Å) and in the related mononuclear macrocyclic species [6-acetyl-7,12,14-trimethyl-3,9-bis(methylsulfanyl)-1,2,4,8,10,11-hexaazacyclotetradeca-2,5,7,9,11,13-hexaenato(2−)-N^1,N^4,N^8,N^{11}]nickel(II) (1.872 and 1.826 Å).[16] This can be explained by taking into account the lack of stacking interactions and/or additional weak nickel–ligand interactions in the crystalline structure. The peripheral substituents of the macrocycle are also able to cause the redistribution of electron density at the nitrogen donors and as a consequence alter the Ni–N bond length.

Two geometrically equivalent macrocycles (in terms of bond lengths and angles) coupled by a single C(7a)(sp^2)–C(7b)(sp^2) bond (1.54 Å) are nearly perpendicular to each other. The dihedral angle between planes (a and b) determined by N(1), N(3), N(4) and N(6) donor atoms is 80.6°. This turn, around the single C–C bond, is caused by steric interactions between the methyl groups [C(11) and C(12)] of both halves of the binuclear species. This effectively prevents delocalization of the π-electron system. Note that the corresponding dihedral angles for molecules A and B of the precursor $[Ni_2L^2]$ are 80.5 and 73.6°, respectively.[13]

Table 2 Atomic positional parameters

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni(a)	0.418 47(9)	0.231 1(1)	0.671 5(2)	C(2b)	0.978 4(8)	0.339 6(10)	0.547 4(19)
Ni(b)	0.848 27(9)	0.277 3(1)	0.657 6(2)	C(3a)	0.245 2(8)	0.218 4(10)	0.651 0(18)
S(1a)	0.354 8(2)	0.054 0(2)	0.381 5(5)	C(3b)	1.020 7(8)	0.291 5(10)	0.627 1(18)
S(1b)	0.905 8(3)	0.458 9(3)	0.372 0(6)	C(4a)	0.274 0(8)	0.270 2(10)	0.742 6(2)
S(2a)	0.314 1(3)	0.396 9(3)	0.938 4(6)	C(4b)	0.994 2(8)	0.238 4(10)	0.719 8(2)
S(2b)	0.956 0(3)	0.110 7(3)	0.919 0(6)	C(5a)	0.373 3(8)	0.337 4(9)	0.851 2(2)
N(1a)	0.490 7(6)	0.182 9(6)	0.582 4(12)	C(5b)	0.894 6(8)	0.169 5(9)	0.832 9(19)
N(1b)	0.774 0(6)	0.326 7(6)	0.575 9(13)	C(6a)	0.551 3(8)	0.296 4(8)	0.767 9(16)
N(2a)	0.468 1(6)	0.124 7(6)	0.486 8(13)	C(6b)	0.717 0(7)	0.211 1(8)	0.760 6(16)
N(2b)	0.795 0(7)	0.386 8(7)	0.483 7(14)	C(7a)	0.592 5(7)	0.249 7(8)	0.678 3(17)
N(3a)	0.357 2(5)	0.170 5(7)	0.571 2(13)	C(7b)	0.675 8(7)	0.259 1(8)	0.676 3(16)
N(3b)	0.906 6(6)	0.338 7(8)	0.552 9(15)	C(8a)	0.562 0(7)	0.195 7(7)	0.585 1(15)
N(4a)	0.344 3(6)	0.282 2(7)	0.757 0(14)	C(8b)	0.703 7(7)	0.314 4(8)	0.585 5(16)
N(4b)	0.922 2(6)	0.225 6(8)	0.737 5(14)	C(9a)	0.433 5(9)	0.012 6(9)	0.298 9(20)
N(5a)	0.442 9(6)	0.345 8(7)	0.861 6(13)	C(9b)	0.827 5(11)	0.505 7(10)	0.309 6(23)
N(5b)	0.826 7(6)	0.162 4(7)	0.847 9(14)	C(10a)	0.376 6(11)	0.459 4(11)	1.019 1(26)
N(6a)	0.477 8(6)	0.290 9(6)	0.770 5(13)	C(10b)	0.894 3(11)	0.056 9(10)	1.021 3(23)
N(6b)	0.790 6(6)	0.217 4(7)	0.659 5(13)	C(11a)	0.588 2(8)	0.353 8(9)	0.861 2(18)
C(1a)	0.398 3(7)	0.120 9(8)	0.485 5(16)	C(11b)	0.684 2(8)	0.152 6(9)	0.857 9(18)
C(1b)	0.863 9(8)	0.389 9(9)	0.473 1(17)	C(12a)	0.611 3(7)	0.152 4(8)	0.483 7(17)
C(2a)	0.286 8(7)	0.171 7(9)	0.568 2(17)	C(12b)	0.651 6(8)	0.361 2(9)	0.496 6(21)

Table 3 Bond lengths (Å) and angles (°) for [Ni_2L^3] with estimated standard deviations in parentheses

Ni(a)–N(1a)	1.79(1)	Ni(b)–N(1b)	1.79(1)	C(3a)–C(4a)	1.37(3)	C(3b)–C(4b)	1.38(3)
Ni(a)–N(6a)	1.78(1)	Ni(b)–N(6b)	1.79(1)	C(4a)–N(4a)	1.31(2)	C(4b)–N(4b)	1.35(2)
Ni(a)–N(3a)	1.82(1)	Ni(b)–N(3b)	1.82(1)	N(4a)–C(5a)	1.43(2)	N(4b)–C(5b)	1.44(2)
Ni(a)–N(4a)	1.82(1)	Ni(b)–N(4b)	1.80(1)	C(5a)–N(5a)	1.28(2)	C(5b)–N(5b)	1.26(2)
S(1a)–C(1a)	1.74(2)	S(1b)–C(1b)	1.74(2)	N(5a)–N(6a)	1.45(2)	N(5b)–N(6b)	1.44(2)
S(2a)–C(5a)	1.73(2)	S(2b)–C(5b)	1.74(2)	N(6a)–C(6a)	1.35(2)	N(6b)–C(6b)	1.35(2)
S(1a)–C(9a)	1.79(2)	S(1b)–C(9b)	1.76(2)	C(6a)–C(7a)	1.40(2)	C(6b)–C(7b)	1.39(2)
S(2a)–C(10a)	1.77(2)	S(2b)–C(10b)	1.77(2)	C(7a)–C(8a)	1.41(2)	C(7b)–C(8b)	1.40(2)
N(1a)–N(2a)	1.43(2)	N(1b)–N(2b)	1.43(2)	C(8a)–N(1a)	1.32(2)	C(8b)–N(1b)	1.31(2)
N(2a)–C(1a)	1.28(2)	N(2b)–C(1b)	1.27(2)	C(8a)–C(12a)	1.52(2)	C(8b)–C(12b)	1.51(2)
C(1a)–N(3a)	1.41(2)	C(1b)–N(3b)	1.42(2)	C(6a)–C(11a)	1.52(2)	C(6b)–C(11b)	1.51(2)
N(3a)–C(2a)	1.29(2)	N(3b)–C(2b)	1.32(2)	C(7a)–C(7b)	1.54(2)		
C(2a)–C(3a)	1.37(2)	C(2b)–C(3b)	1.38(2)				
N(1a)–Ni(a)–N(3a)	85.8(5)	N(1b)–Ni(b)–N(3b)	85.3(6)	Ni(a)–N(6a)–C(6a)	129.9(10)	Ni(b)–N(6b)–C(6b)	130.3(10)
N(1a)–Ni(a)–N(4a)	178.1(5)	N(1b)–Ni(b)–N(4b)	178.5(6)	N(5a)–N(6a)–C(6a)	113.6(11)	N(5b)–N(6b)–C(6b)	113.0(11)
N(1a)–Ni(a)–N(6a)	94.6(5)	N(1b)–Ni(b)–N(6b)	94.3(5)	S(1a)–C(1a)–N(2a)	119.8(11)	S(1b)–C(1b)–N(2b)	120.9(12)
N(3a)–Ni(a)–N(4a)	93.8(5)	N(3b)–Ni(b)–N(4b)	95.3(6)	S(1a)–C(1a)–N(3a)	120.5(10)	S(1b)–C(1b)–N(3b)	120.2(11)
N(3a)–Ni(a)–N(6a)	179.5(5)	N(3b)–Ni(b)–N(6b)	179.6(6)	N(2a)–C(1a)–N(3a)	119.5(12)	N(2b)–C(1b)–N(3b)	118.7(14)
N(4a)–Ni(a)–N(6a)	85.7(5)	N(4b)–Ni(b)–N(6b)	85.0(6)	N(3a)–C(2a)–C(3a)	123.7(14)	N(3b)–C(2b)–C(3b)	122.1(16)
C(1a)–S(1a)–C(9a)	99.1(7)	C(1b)–S(1b)–C(9b)	99.1(9)	C(2a)–C(3a)–C(4a)	123.5(15)	C(2b)–C(3b)–C(4b)	125.0(16)
C(5a)–S(2a)–C(10a)	100.8(9)	C(5b)–S(2b)–C(10b)	99.6(9)	N(4a)–C(4a)–C(3a)	123.5(15)	N(4b)–C(4b)–C(3b)	122.8(15)
Ni(a)–N(1a)–N(2a)	115.3(8)	Ni(b)–N(1b)–N(2b)	115.0(9)	S(2a)–C(5a)–N(4a)	119.1(11)	S(2b)–C(5b)–N(4b)	119.0(11)
Ni(a)–N(1a)–C(8a)	129.4(10)	Ni(b)–N(1b)–C(8b)	129.1(10)	S(2a)–C(5a)–N(5a)	120.9(12)	S(2b)–C(5b)–N(5b)	121.7(13)
N(2a)–N(1a)–C(8a)	115.0(11)	N(2b)–N(1b)–C(8b)	115.7(11)	N(4a)–C(5a)–N(5a)	119.6(13)	N(4b)–C(5b)–N(5b)	119.2(14)
N(1a)–N(2a)–C(1a)	109.4(11)	N(1b)–N(2b)–C(1b)	110.3(12)	N(6a)–C(6a)–C(7a)	120.1(13)	N(6b)–C(6b)–C(7b)	118.9(13)
Ni(a)–N(3a)–C(1a)	109.8(9)	Ni(b)–N(3b)–C(1b)	110.4(10)	N(6a)–C(6a)–C(11a)	119.0(13)	N(6b)–C(6b)–C(11b)	117.4(12)
Ni(a)–N(3a)–C(2a)	127.9(10)	Ni(b)–N(3b)–C(2b)	128.0(12)	C(7a)–C(6a)–C(11a)	120.7(13)	C(7b)–C(6b)–C(11b)	123.6(13)
C(1a)–N(3a)–C(2a)	122.1(12)	C(1b)–N(3b)–C(2b)	121.4(14)	C(6a)–C(7a)–C(7b)	118.3(12)	C(6b)–C(7b)–C(7a)	117.5(12)
Ni(a)–N(4a)–C(4a)	127.1(11)	Ni(b)–N(4b)–C(4b)	126.5(11)	C(6a)–C(7a)–C(8a)	124.1(13)	C(6b)–C(7b)–C(8b)	125.6(13)
Ni(a)–N(4a)–C(5a)	109.9(9)	Ni(b)–N(4b)–C(5b)	110.6(10)	C(7b)–C(7a)–C(8a)	117.3(12)	C(7a)–C(7b)–C(8b)	116.8(12)
C(4a)–N(4a)–C(5a)	122.7(13)	C(4b)–N(4b)–C(5b)	122.7(13)	N(1a)–C(8a)–C(7a)	121.2(12)	N(1b)–C(8b)–C(7b)	121.4(13)
N(6a)–N(5a)–C(5a)	108.3(11)	N(6b)–N(5b)–C(5b)	108.6(12)	N(1a)–C(8a)–C(12a)	119.0(12)	N(1b)–C(8b)–C(12b)	119.0(13)
Ni(a)–N(6a)–N(5a)	116.2(8)	Ni(b)–N(6b)–N(5b)	116.4(9)	C(7a)–C(8a)–C(12a)	119.6(12)	C(7b)–C(8b)–C(12b)	119.4(13)

Two five-membered NiN_3C and two six-membered NiN_2C_3 rings are formed in each half of the binuclear unit. The five-membered rings are planar. All four SMe groups are *cis*-positioned relative to the N–C bond in each five-membered ring. The mean N–N, N–C and C–N distances (1.430, 1.275 and 1.415 Å) in the NiN_3C ring are similar to those of related co-ordinated isothiosemicarbazones.[16,17] The S–C and S–CH_3 bond lengths are 1.74 and 1.77 Å, and the angle at sulfur is 99.7°. The six-membered ring NiN(3)C(2)C(3)C(4)N(4) is planar with mean distances N–C 1.32, C–C 1.37 Å and the angle C(2)–C(3)–C(4) 124°. This angle indicates sp^2 hybridization for the C(3) atom. The second six-membered metallocycle is also planar. The methyl groups deviate considerably from the planes of the corresponding rings: C(12a) by 0.141 and C(12b) by 0.053 Å. The corresponding distances in these metallocycles are very close to those reported in other related structures.

The ^1H NMR spectrum consists of four distinct signals with resonances attributable to CH=N (doublet), =CH (triplet), SCH_3 (singlet) and CH_3 (singlet). The number of signals and their relative areas indicate the chemical equivalence of both

Table 4 Absorption maxima and molar absorption coefficients in $CHCl_3$

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
[Ni_2L^3]	755 (sh) (1 430), 692 (1 780), 637 (sh) (1 490), 506 (9 560), 480 (8 270), 417 (15 140), 367 (29 135), 353 (27 640), 324 (sh) (35 600), 307 (44 070)
[NiL^4]	735 (sh) (630), 670 (820), 620 (sh) (700), 503 (4 160), 478 (3 770), 411 (5 220), 357 (12 470), 345 (12 570), 320 (14 500), 300 (15 080)

halves of the two-compartmental molecules in solution. The chemical shifts of all the protons in [Ni_2L^3] remain almost unchanged when compared with corresponding resonances of the mononuclear analogue [NiL^4][H_2L^4 = 12,14-dimethyl-3,9-bis(methylsulfanyl)-1,2,4,8,10,11-hexaazacyclotetradeca-2,4,6,9,11,13-hexaene].[18]

The electronic absorption bands of the binuclear complex [Ni_2L^3] in comparison with that of the mononuclear [NiL^4] are given in Table 4. The main peculiarity of the data presented is the similarity of the spectra in the region 800–300 nm. The molar absorptivities of [Ni_2L^3] are practically the sum of those of [NiL^4]. This fact is evidence of the structural similarity of the co-ordination polyhedron(s) in the mono macrocyclic complex [NiL^4] which in fact is a half of the binuclear derivative, and [Ni_2L^3].

Conclusion

A simple and efficient route to assemble ditopic transition-metal complexes based on 3-alkylisothiosemicarbazide ligands has been proposed. An X-ray diffraction study has shown that two geometrically equivalent macrocyclic subunits (in terms of bond lengths and angles) are nearly perpendicular to each other, due to steric interactions between the methyl groups of both halves of the binuclear units. This effectively prevents delocalization of the π-electron system. As a consequence (according to ^{1}H NMR and UV/VIS data) there is little mutual interaction of the two subunits.

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