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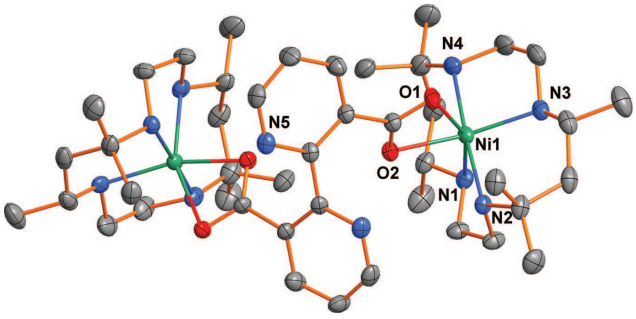
Crystal structure of (μ_2-2,2′-bipyridine-3,3′-dicarboxylato)-bis(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-di-nickel(II) perchlorate *N,N′*-dimethylformamide solvate, $C_{50}H_{92}Cl_2N_{12}Ni_2O_{14}$



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Abstract

$C_{50}H_{92}Cl_2N_{12}Ni_2O_{14}$, monoclinic, $C2/c$ (no. 15), $a = 25.731(5)$ Å, $b = 9.940(2)$ Å, $c = 26.574(5)$ Å, $\beta = 114.825(4)°$, $V = 6169(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0675$, $wR_{ref}(F^2) = 0.2209$, $T = 173(2)$ K.

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The cationic complex of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

An acetonitrile solution (20 mL) of [Ni(rac-*L*)]$(ClO_4)_2$ (0.270 g, 0.5 mmol) (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane) was added to a solution of 2,2′-bipyridine-3,3′-dicarboxylic acid (0.060 g, 0.25 mmol) and NaOH (0.02 g, 0.5 mmol) in the minimum amount of water and DMF (1:1). After a few days, blue prism-shaped crystals were separated

Table 1: Data collection and handling.

Crystal:	Clear blue block
Size:	0.41 × 0.35 × 0.32 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.77 mm^{-1}
Diffractometer, scan mode:	CCD area detrector, φ and ω-scans
θ_{max}, completeness:	27°, >96%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14245, 6563, 0.046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4169
$N(param)_{refined}$:	364
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3], DIAMOND [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Ni1	0.60021(2)	0.53484(6)	0.40671(2)	0.0268(2)
O2	0.54677(13)	0.6012(3)	0.32682(12)	0.0285(7)
O1	0.63496(13)	0.6753(3)	0.36734(12)	0.0347(8)
N2	0.55806(16)	0.6811(4)	0.43503(15)	0.0292(8)
H2	0.53482(16)	0.7287(4)	0.40345(15)	0.0351(10)*
N5	0.51463(18)	0.8679(4)	0.19326(15)	0.0336(9)
N3	0.66871(16)	0.5240(4)	0.48508(15)	0.0340(9)
H3	0.65848(16)	0.4647(4)	0.50646(15)	0.0408(11)*
N1	0.53853(16)	0.4026(4)	0.40970(15)	0.0311(9)
H1	0.55386(16)	0.3566(4)	0.44327(15)	0.0374(10)*
N4	0.64351(17)	0.3817(4)	0.38297(16)	0.0359(9)
H4	0.66140(17)	0.4253(4)	0.36356(16)	0.0431(11)*
C22	0.52415(19)	0.8087(4)	0.24194(17)	0.0263(9)
C18	0.57745(19)	0.7527(4)	0.27568(18)	0.0287(10)
C17	0.58667(19)	0.6734(4)	0.32675(18)	0.0287(10)
C15	0.5187(2)	0.3026(5)	0.36346(19)	0.0341(11)
H15	0.5049(2)	0.3532(5)	0.32766(19)	0.0409(13)*
C2	0.5180(2)	0.6020(5)	0.4502(2)	0.0376(11)
H2a	0.5387(2)	0.5639(5)	0.4878(2)	0.0451(14)*
H2b	0.4871(2)	0.6610(5)	0.4503(2)	0.0451(14)*
C3	0.5906(2)	0.7866(5)	0.47677(19)	0.0376(12)
C1	0.4928(2)	0.4902(5)	0.4089(2)	0.0365(11)
H1a	0.4718(2)	0.5284(5)	0.3713(2)	0.0438(14)*
H1b	0.4654(2)	0.4378(5)	0.4183(2)	0.0438(14)*
C21	0.5574(2)	0.8707(5)	0.1776(2)	0.0384(12)
H21	0.5504(2)	0.9101(5)	0.1427(2)	0.0461(14)*
C11	0.6109(2)	0.2669(5)	0.3469(2)	0.0431(13)
C14	0.5671(2)	0.2117(5)	0.3667(2)	0.0427(13)
H14a	0.5882(2)	0.1834(5)	0.4058(2)	0.0512(15)*
H14b	0.5499(2)	0.1298(5)	0.3448(2)	0.0512(15)*

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Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C19	0.6216(2)	0.7625(5)	0.2594(2)	0.0415(12)
H19	0.6587(2)	0.7301(5)	0.2827(2)	0.0498(15)*
C12	0.5813(2)	0.3200(6)	0.2874(2)	0.0433(13)
H12a	0.5571(13)	0.397(2)	0.2863(3)	0.0650(19)*
H12b	0.6103(2)	0.348(3)	0.2747(6)	0.0650(19)*
H12c	0.5576(12)	0.2488(13)	0.2631(3)	0.0650(19)*
C20	0.6110(2)	0.8204(6)	0.2085(2)	0.0426(13)
H20	0.6401(2)	0.8250(6)	0.1954(2)	0.0511(15)*
C4	0.6136(2)	0.8863(5)	0.4473(2)	0.0446(13)
H4a	0.6354(14)	0.8376(7)	0.4305(13)	0.067(2)*
H4b	0.5816(3)	0.934(3)	0.4184(10)	0.067(2)*
H4c	0.6386(13)	0.952(2)	0.4743(3)	0.067(2)*
C7	0.6883(2)	0.6518(5)	0.5171(2)	0.0404(12)
H7	0.7011(2)	0.7147(5)	0.4952(2)	0.0485(15)*
C10	0.6901(2)	0.3391(6)	0.4363(2)	0.0487(14)
H10a	0.6750(2)	0.2736(6)	0.4549(2)	0.0584(17)*
H10b	0.7207(2)	0.2944(6)	0.4292(2)	0.0584(17)*
C6	0.6392(2)	0.7190(5)	0.52608(19)	0.0420(13)
H6a	0.6563(2)	0.7879(5)	0.55534(19)	0.0504(15)*
H6b	0.6218(2)	0.6498(5)	0.54099(19)	0.0504(15)*
C9	0.7143(2)	0.4590(6)	0.4733(2)	0.0483(14)
H9a	0.7298(2)	0.5241(6)	0.4549(2)	0.0580(17)*
H9b	0.7459(2)	0.4300(6)	0.5084(2)	0.0580(17)*
C5	0.5526(3)	0.8609(6)	0.4985(2)	0.0509(14)
H5a	0.5176(8)	0.890(4)	0.4673(2)	0.076(2)*
H5b	0.5427(14)	0.8007(14)	0.5224(14)	0.076(2)*
H5c	0.5732(7)	0.939(2)	0.5200(14)	0.076(2)*
C8	0.7384(2)	0.6284(7)	0.5733(2)	0.0618(18)
H8a	0.7261(6)	0.570(4)	0.5960(8)	0.093(3)*
H8b	0.7699(8)	0.585(4)	0.5679(3)	0.093(3)*
H8c	0.7514(13)	0.7149(8)	0.5922(8)	0.093(3)*
C13	0.6507(3)	0.1518(6)	0.3476(3)	0.0622(18)
H13a	0.6843(10)	0.1886(7)	0.3439(19)	0.093(3)*
H13b	0.6631(16)	0.103(3)	0.3826(8)	0.093(3)*
H13c	0.6303(7)	0.091(3)	0.3166(12)	0.093(3)*
N6	0.7654(2)	0.5708(6)	0.2822(3)	0.0635(15)
C16	0.4692(3)	0.2170(6)	0.3631(3)	0.0562(16)
H16a	0.4825(5)	0.162(3)	0.3968(9)	0.084(2)*
H16b	0.4381(8)	0.2759(6)	0.3616(18)	0.084(2)*
H16c	0.4553(12)	0.158(3)	0.3305(10)	0.084(2)*
O3	0.7069(2)	0.4493(6)	0.3076(2)	0.0921(18)
C25	0.7502(3)	0.5140(7)	0.3186(3)	0.0611(17)
H25	0.7753(3)	0.5244(7)	0.3567(3)	0.073(2)*
C23	0.7314(4)	0.5592(11)	0.2235(4)	0.108(3)
H23a	0.7514(16)	0.502(6)	0.2072(6)	0.161(5)*
H23b	0.6943(14)	0.519(7)	0.2167(4)	0.161(5)*
H23c	0.726(3)	0.6487(14)	0.2065(6)	0.161(5)*
C24	0.8202(4)	0.6416(9)	0.3013(5)	0.111(3)
H24a	0.8398(15)	0.636(6)	0.3418(5)	0.167(5)*
H24b	0.8440(13)	0.600(5)	0.285(2)	0.167(5)*
H24c	0.8134(4)	0.736(2)	0.290(3)	0.167(5)*
O6[a]	0.6280(4)	0.1409(11)	0.5992(4)	0.0911(12)
O5[a]	0.5859(3)	0.2203(10)	0.5089(3)	0.0911(12)
O7[a]	0.6816(3)	0.2023(10)	0.5497(4)	0.0911(12)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
O4[a]	0.6312(4)	0.3701(7)	0.5764(4)	0.0911(12)
Cl1[a]	0.63675(6)	0.23180(14)	0.56349(5)	0.0460(4)
Cl1a[b]	0.63675(6)	0.23180(14)	0.56349(5)	0.0460(4)
O7a[b]	0.6856(4)	0.3044(12)	0.6041(4)	0.0911(12)
O5a[b]	0.6012(5)	0.3200(13)	0.5229(5)	0.0911(12)
O6a[b]	0.6666(6)	0.1342(12)	0.5425(6)	0.0911(12)
O4a[b]	0.6092(6)	0.1521(16)	0.5896(7)	0.0911(12)

Occupancies: [a] = 0.606(5), [b] = 0.395(5)

in ~25% yield. Anal. calcd. for $C_{50}H_{92}Cl_2N_{12}Ni_2O_{14}$: C, 47.15; H, 7.28; N, 13.19%. Found: C, 47.42; H, 7.26; N, 13.65%.

Experimental details

H atoms were positioned geometrically and were included in the refinement in the riding-model approximation. The ClO_4^- anion is disordered over two sites.

Discussion

Extended bridged dinuclear complexes such as those with terephthalate, oxalate, butene dicarboxylate and succinate have been synthesized [5–10].

Single crystal structural analysis displays that the title compound contains one $[(NiL)_2(C_{12}H_6N_2O_4)]^{2+}$, two ClO_4^- and two DMF molecules. Two $[NiL]^{2+}$ units are bridged by one $[C_{12}H_6N_2O_4]^{2-}$ anion to form the dimer. In the dimer, the two Ni(II) atoms display a distorted octahedral coordination geometry by coordination with four nitrogen atoms of the macrocyclic ligand in a folded conformation, plus two carboxylate oxygen atoms of $[C_{12}H_6N_2O_4]^{2-}$. The Ni—N bond lengths 2.088(4)—2.132(4) Å are slightly shorter than the Ni—O bond lengths 2.093(3) and 2.152(3) Å.

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