Instrumental Achievements

Crystal Structure of $[Ni_3(dpa)_4(NO_3)_2]$: Axial Replacement of Metal String Complexes

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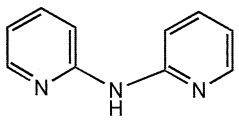
Linear metal string complexes have attracted much attention because of potential applications of molecule-based magnetic and electronic materials. Six linear tri-nuclear di-(2-pyridyl)amine (Hdpa) complexes containing Ni, Cu, Co, Cr, Ru and Rh atoms have been reported since 1990.[1] In recent years several research projects were conducted to replace the axial ligands of metal string complexes by such molecules as NCS^-, BF_4^-, $N(CN)_2^-$, N_3^- and PF_6^-.[2] An axial replacement can tune the metal-metal distances of the metal string complexes. The first trinuclear complex with a nitrate axial ligand is reported in this context.



Scheme 1

The crystal structure of the title compound is shown in Fig. 1. Crystal and experimental data are listed in Table 1. The atomic coordinates, equivalent isotropic displacement parameters and occupancies are given in Table 2. The structure is a linear trimetallic unit with a spiral arrangement of four dipyridylamido ligands. The spiral arrangement results from steric crowding of the β-carbon hydrogen atoms on the pyridyl rings. In the title complex the Ni-Ni bonds of 2.3982(5) and 2.4074(5)Å are slightly shorter than that of $Ni_3(dpa)_4Cl_2$. The NO_3^- anions in the $[Ni_3(dpa)_4]^{2+}$ chromophe occupy the axial coordination sites of the two terminal nickel atoms. Ignoring the Ni–Ni separations, the central Ni atom is four-coordinated with a rhombohedral geometry and involves the four independent deprotonated nitrogen atoms of the dpa anions. Usually in low-spin square co-planar nickel systems, the Ni–N distance is about 1.90 Å, which is comparable to the mean Ni–N distance of 1.892(3)Å in the title complex. The terminal nickel atoms are five-coordinate, square pyramidal, giving a slight rhombohedral component, NiN_4O chromophome. The mean Ni–N distance, 2.086(2)Å, is significantly longer than those of the central NiN_4 environment, but is consistent with the equatorial Ni–N distances of 2.0 – 2.1 Å usually found in square-based pyramidal nickel(II) compounds. The axial Ni–O distance is 2.043(2)Å. Obviously, the terminal nickel atoms have high spin and the

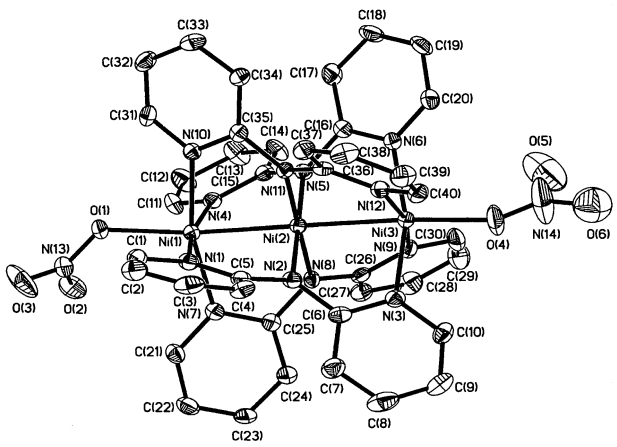


Fig. 1 Crystal structure of $[Ni_3(dpa)_4(NO_3)_2]$.

Table 1 Crystal and experimental data

Formula: $C_{40}H_{32}N_{14}Ni_3O_6$
Formula weight = 980.93
Crystal system: orthorhombic
Space group: $P2_12_12_1$ $Z = 4$
a = 13.8992(3)Å
b = 16.5637(4)Å
c = 17.6535(4)Å
V = 4064.23(16)Å^3
D_x = 1.603 g/cm^3
μ(MoK$_\alpha$) = 1.443 mm^{-1}
T = 150(2)K
R = 0.0328
wR = 0.0716
$(\Delta\rho)_{max}$ = 0.939 eÅ^{-3}
$(\Delta\rho)_{min}$ = –0.568 eÅ^{-3}
No. of reflections used = 9327
No. of parameters refined = 569
Goodness-of-fit on F^2 = 1.060
Measurement: Brucker Smart CCD
Program system: Bruker SHELXTL
Structure determination: SHELXL-97
Refinement: full-matrix

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Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*x*	*y*	*z*	U_{eq}	occ
Ni(1)	0.89543(3)	0.69291(2)	0.82634(2)	0.01536(9)	1
Ni(2)	0.74508(3)	0.71901(2)	0.76437(2)	0.01408(8)	1
Ni(3)	0.59350(3)	0.74315(2)	0.70240(2)	0.01712(9)	1
N(1)	0.95309(17)	0.70387(14)	0.71786(14)	0.0193(6)	1
N(2)	0.79803(17)	0.68086(14)	0.67198(15)	0.0178(5)	1
N(3)	0.64464(19)	0.65715(15)	0.62547(14)	0.0193(6)	1
N(4)	0.81321(17)	0.69060(15)	0.92375(13)	0.0175(5)	1
N(5)	0.69338(16)	0.75787(15)	0.85637(13)	0.0161(5)	1
N(6)	0.57999(17)	0.82892(14)	0.78725(14)	0.0175(5)	1
N(7)	0.86155(17)	0.57342(14)	0.79941(15)	0.0171(5)	1
N(8)	0.70265(17)	0.61457(14)	0.78934(14)	0.0163(5)	1
N(9)	0.54424(17)	0.65475(15)	0.77664(14)	0.0192(6)	1
N(10)	0.89690(18)	0.81950(14)	0.83721(14)	0.0174(5)	1
N(11)	0.78694(17)	0.82500(14)	0.73926(14)	0.0159(5)	1
N(12)	0.67435(18)	0.82873(15)	0.64198(14)	0.0191(6)	1
N(13)	1.0789(2)	0.62448(17)	0.89025(16)	0.0279(7)	1
N(14)	0.3938(3)	0.7830(3)	0.6406(2)	0.0764(15)	1
O(1)	1.02822(15)	0.68838(13)	0.87578(12)	0.0235(5)	1
O(2)	1.04396(18)	0.56915(14)	0.92845(14)	0.0335(6)	1
O(3)	1.16096(19)	0.62195(18)	0.8649(2)	0.0644(10)	1
O(4)	0.47487(16)	0.76175(17)	0.63739(14)	0.0414(7)	1
O(5)	0.3553(3)	0.7942(2)	0.7080(3)	0.0953(13)	1
O(6)	0.3321(4)	0.7902(4)	0.5983(3)	0.076(2)	0.668
O(6')	0.3818(9)	0.8479(8)	0.5965(7)	0.085(5)	0.332
C(1)	1.0460(2)	0.72432(18)	0.70667(19)	0.0229(7)	1
C(2)	1.0838(2)	0.7428(2)	0.63696(19)	0.0297(8)	1
C(3)	1.0216(2)	0.7426(2)	0.57547(19)	0.0289(8)	1
C(4)	0.9272(2)	0.72118(19)	0.58471(17)	0.0239(7)	1
C(5)	0.8935(2)	0.70001(7)	0.65697(17)	0.0193(6)	1
C(6)	0.7407(2)	0.64378(17)	0.61973(16)	0.0198(7)	1
C(7)	0.7760(2)	0.5895(2)	0.56411(19)	0.0280(8)	1
C(8)	0.7140(3)	0.5536(2)	0.5147(2)	0.0361(9)	1
C(9)	0.6159(3)	0.5687(2)	0.51965(19)	0.0310(8)	1
C(10)	0.5849(2)	0.61925(18)	0.57654(18)	0.0234(7)	1
C(11)	0.8467(2)	0.6579(2)	0.98845(18)	0.0235(7)	1
C(12)	0.7975(3)	0.6595(2)	1.05633(19)	0.0311(8)	1
C(13)	0.7066(2)	0.6953(2)	1.05722(18)	0.0295(8)	1
C(14)	0.6704(2)	0.7280(2)	0.99163(17)	0.0248(7)	1
C(15)	0.7252(2)	0.72710(17)	0.92468(16)	0.0181(6)	1
C(16)	0.6326(2)	0.82350(18)	0.85177(17)	0.0169(6)	1
C(17)	0.6284(2)	0.8854(2)	0.90597(18)	0.0253(8)	1
C(18)	0.5716(3)	0.9520(2)	0.8924(2)	0.0306(8)	1
C(19)	0.5204(2)	0.9584(2)	0.8251(2)	0.0296(8)	1
C(20)	0.5268(2)	0.89619(18)	0.77450(19)	0.0226(7)	1
C(21)	0.9305(2)	0.51690(18)	0.78931(18)	0.0213(7)	1
C(22)	0.9119(2)	0.43762(19)	0.77277(19)	0.0258(7)	1
C(23)	0.8158(2)	0.41470(18)	0.7648(2)	0.0257(7)	1
C(24)	0.7446(2)	0.47145(17)	0.77114(18)	0.0235(7)	1
C(25)	0.7685(2)	0.55161(17)	0.78799(16)	0.0174(6)	1
C(26)	0.6075(2)	0.60243(17)	0.80839(16)	0.0184(6)	1
C(27)	0.5761(2)	0.54515(19)	0.86126(18)	0.0228(7)	1
C(28)	0.4803(2)	0.5409(2)	0.8803(2)	0.0294(8)	1
C(29)	0.4158(2)	0.5945(2)	0.8484(2)	0.0338(8)	1
C(30)	0.4509(2)	0.6505(2)	0.7981(2)	0.0288(8)	1
C(31)	0.9482(2)	0.85647(19)	0.89214(18)	0.0212(7)	1
C(32)	0.9524(2)	0.9385(2)	0.90103(19)	0.0265(8)	1
C(33)	0.8988(2)	0.98667(19)	0.85148(17)	0.0255(7)	1
C(34)	0.8433(2)	0.95097(18)	0.79763(18)	0.0194(6)	1
C(35)	0.8437(2)	0.86632(18)	0.78960(17)	0.0171(6)	1
C(36)	0.7586(2)	0.85681(16)	0.67081(17)	0.0170(6)	1
C(37)	0.8149(2)	0.91178(19)	0.62843(18)	0.0223(7)	1
C(38)	0.7840(3)	0.93596(19)	0.55820(19)	0.0274(8)	1
C(39)	0.6989(3)	0.9060(2)	0.52872(19)	0.0287(8)	1
C(40)	0.6469(2)	0.85243(19)	0.57304(18)	0.0239(7)	1

Table 3 Selected bond distances (Å) and angles (°)

Ni(1)-O(1)	2.043(2)	Ni(1)-N(1)	2.084(2)
Ni(1)-N(4)	2.065(2)	Ni(1)-N(7)	2.089(2)
Ni(1)-N(10)	2.106(2)	Ni(1)-Ni(2)	2.3982(5)
Ni(2)-N(2)	1.898(3)	Ni(2)-N(5)	1.889(2)
Ni(2)-N(8)	1.880(2)	Ni(2)-N(11)	1.902(2)
Ni(2)-Ni(3)	2.4074(5)	Ni(3)-O(4)	2.032(2)
Ni(3)-N(3)	2.093(3)	Ni(3)-N(6)	2.073(2)
Ni(3)-N(9)	2.081(3)	Ni(3)-N(12)	2.100(3)
O(1)-Ni(1)-N(1)	92.77(9)	O(1)-Ni(1)-N(4)	98.26(9)
O(1)-Ni(1)-N(7)	105.43(9)	O(1)-Ni(1)-N(10)	89.36(9)
O(1)-Ni(1)-Ni(2)	171.40(7)	N(1)-Ni(1)-N(4)	168.42(10)
N(1)-Ni(1)-N(7)	87.71(10)	N(1)-Ni(1)-N(10)	89.61(10)
N(1)-Ni(1)-Ni(2)	84.27(7)	N(4)-Ni(1)-N(7)	92.71(10)
N(4)-Ni(1)-N(10)	87.02(10)	N(4)-Ni(1)-Ni(2)	84.31(7)
N(7)-Ni(1)-N(10)	165.07(10)	N(7)-Ni(1)-Ni(2)	82.56(7)
Ni(1)-Ni(2)-Ni(3)	179.16(2)	Ni(1)-Ni(2)-N(2)	89.66(8)
Ni(1)-Ni(2)-N(5)	90.04(7)	Ni(1)-Ni(2)-N(8)	90.03(7)
Ni(1)-Ni(2)-N(11)	90.35(7)	N(2)-Ni(2)-N(5)	179.38(11)
N(2)-Ni(2)-N(8)	90.96(11)	N(2)-Ni(2)-N(11)	89.33(10)
N(5)-Ni(2)-N(8)	89.58(11)	N(5)-Ni(2)-N(11)	90.13(11)
N(8)-Ni(2)-N(11)	179.52(11)	Ni(2)-Ni(3)-O(4)	172.65(7)
N(3)-Ni(3)-N(6)	165.07(10)	N(3)-Ni(3)-N(9)	92.38(10)
N(3)-Ni(3)-N(12)	87.03(10)	N(6)-Ni(3)-N(9)	89.85(9)
N(6)-Ni(3)-N(12)	87.30(10)	N(9)-Ni(3)-N(12)	166.14(10)
O(4)-Ni(3)-N(3)	90.71(10)	O(4)-Ni(3)-N(6)	103.34(10)
O(4)-Ni(3)-N(9)	101.27(10)	O(4)-Ni(3)-N(12)	92.58(10)
N(13)-O(1)-Ni(1)	127.24(19)	N(14)-O(4)-Ni(3)	142.3(3)

central nickel atom has low spin, which is consistent with other nickel string complexes.[3]

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