Crystal Structure of (2,2'-Bipyridine-*N,N'*)(2,2',2''-Triaminotriethylamine-*N,N',N'',N'''*)nickel(II) Diperchlorate

Yung-Chan LIN,** Tian-Huey LU,*† Fen-Ling LIAO,** and Chung-Sun CHUNG**

*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, R. O. C.

**Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, R. O. C.

An X-ray structure determination shows that the Ni(II) ion is a distorted six-coordinated octahedron by four nitrogen atoms of the tetradentate tren ligand constituting the equatorial square base, and by two nitrogen atoms of the bidentate bpy ligand in a *cis* position. The two six-membered rings of bpy are coplanar and almost parallel. The tetradentate ligand consists of three five-membered chelate rings in *gauche* conformations. The Ni-N(tren) bond lengths of this complex are almost equivalent to the reported values.

(Received April 25, 2002; Accepted January 6, 2003)

Understanding the effect of coordinated ligands on the kinetics of ternary complex formation is very significant, since many catalytic reactions need metals, including a wide range of metal enzyme reactions.¹ In the present paper, we report on the crystal structure of a Ni(II) complex (Fig. 1) that contains the tetradentate ligand, 2,2',2''-triaminotriethylamine (tren), and the bidentate ligand, 2,2'-bipyridine (bpy), to expand knowledge in this area.

To a solution of Ni(ClO₄)₂·6H₂O (1.24 g, 3.4 mmol in ethanol, 100 ml), a solution of tren (0.50 g, 3.4 mmol in ethanol, 50 ml) was added drop-wise with stirring. The color of the solution changed from green to blue. The reaction mixture was stirred continuously for 2 h and then kept for 5 h. A crystal of Ni(tren)(ClO₄)₂ was formed and filtered off. To a solution of Ni(tren)(ClO₄)₂ (0.967 g, 2.4 mmol in ethanol, 50 ml), a solution of bpy (0.40 g, 2.5 mmol in ethanol, 50 ml) was added drop-wise with stirring. The reaction mixture was stirred continuously for 3 h. Violet crystals were precipitated out, and recrystallized from 1:2 CH₃CN-H₂O.

An X-ray structure determination showed that the Ni(II) ion is six-coordinated by four nitrogen atoms of the tetradentate tren ligand and by two nitrogen atoms of the bidentate bpy ligand in a *cis* position (Fig. 2). The coordinated geometry is a distorted

octahedron, as evidenced by the deviation from 90 and 180° of the angles about the central metal ion. The two six-membered

Table 1 Crystal and experimental data

Empirical formula	C ₁₆ H ₂₆ C ₁₂ N ₆ NiO ₈
Formula weight	560.04
Temperature	296(2)K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 10.8840(18) Å <i>b</i> = 14.704(3) Å <i>c</i> = 14.305(2) Å <i>β</i> = 94.29(2)°
Volume	2282.9(7) Å ³
<i>Z</i>	4
Calculated density	1.629 Mg/m ³
Absorption coefficient	1.140 mm ⁻¹
<i>F</i> (0 0 0)	1160
Color	violet
Crystal shape	plate
Crystal size	0.35 × 0.31 × 0.29 mm
<i>θ</i> range for data collection	1.87 to 27.42°
Limiting indices	-14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 19, 0 ≤ <i>l</i> ≤ 18
No. of reflections measured	5530
Refinement method	full-matrix least squares on <i>F</i> ² (SHELXL-97)
Data/restraints/parameters	5231/1/325
Goodness-of-fit on <i>F</i> ²	1.351
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0518 (on <i>F</i>), <i>R</i> _w = 0.1689 (on <i>F</i> ²)
<i>R</i> indices (all data)	<i>R</i> = 0.0753, <i>R</i> _w = 0.1793
Extinction coefficient	0.0058(13)
Largest diff. peak and hole	0.977 (around CL2) and -0.560 e Å ⁻³
(Δσ) _{max} final cycle	0.008
Measurement	Enraf-Nonius CAD4
Program system	NRCVAX
Structure determination	direct methods (SHELXS-97)

Fig. 1 Structural chemical diagram.

† To whom correspondence should be addressed.
E-mail: thlu@phys.nthu.edu.tw

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
Ni	2436(1)	565(1)	7250(1)	35(1)
Cl(1)	-1033(1)	1944(1)	5175(1)	56(1)
Cl(2)	3481(1)	3775(1)	6422(1)	52(1)
O(11)	7(5)	1488(4)	4904(4)	107(2)
O(12)	-970(20)	1910(20)	6193(12)	156(11)
O(12P)	-1340(20)	1650(19)	6032(14)	155(10)
O(13)	-2089(5)	1618(5)	4655(6)	161(3)
O(14)	-992(6)	2883(3)	4954(5)	133(2)
O(21)	3998(5)	3329(4)	7233(3)	119(2)
O(22)	4333(5)	4222(4)	5893(4)	129(2)
O(23)	2504(7)	4289(6)	6546(7)	196(4)
O(24)	3320(30)	3050(10)	5805(11)	167(10)
O(24P)	2840(30)	3124(14)	5878(13)	208(12)
N(1)	3163(3)	-744(2)	7562(3)	51(1)
N(2)	1540(3)	330(2)	8495(2)	47(1)
N(3)	732(3)	49(3)	6627(2)	57(1)
N(4)	1736(4)	1891(2)	7392(3)	58(1)
N(5)	3260(3)	767(2)	6004(2)	42(1)
N(6)	4254(3)	1114(2)	7722(2)	42(1)
C(1)	2717(5)	-1101(3)	8453(3)	65(1)
C(2)	2340(5)	-303(3)	9053(3)	60(1)
C(3)	302(4)	-60(4)	8280(3)	67(1)
C(4)	156(6)	-496(5)	7305(4)	92(2)
C(5)	1446(5)	1238(3)	8936(3)	63(1)
C(6)	998(5)	1926(4)	8218(4)	74(1)
C(7)	4738(4)	1301(3)	8604(3)	55(1)
C(8)	5915(4)	1596(3)	8808(3)	64(1)
C(9)	6680(4)	1686(4)	8095(4)	72(1)
C(10)	6203(4)	1508(3)	7188(3)	62(1)
C(11)	4984(3)	1238(2)	7025(3)	43(1)
C(12)	4414(3)	1086(2)	6063(3)	42(1)
C(13)	5027(4)	1287(3)	5268(3)	62(1)
C(14)	4438(5)	1166(4)	4409(3)	69(1)
C(15)	3261(5)	833(4)	4337(3)	66(1)
C(16)	2705(4)	640(3)	5141(3)	55(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The occupancies of O(12) and O(24) are both 0.48(3), and those of O(12P) and O(24P) are both 0.52(3).

Table 3 Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]

Ni-N(5)	2.075(3)
Ni-N(4)	2.109(3)
Ni-N(1)	2.116(3)
Ni-N(2)	2.122(3)
Ni-N(3)	2.137(3)
Ni-N(6)	2.196(3)
N(5)-Ni-N(4)	97.68(13)
N(5)-Ni-N(1)	97.62(13)
N(4)-Ni-N(1)	162.30(14)
N(5)-Ni-N(2)	177.82(12)
N(4)-Ni-N(2)	82.95(14)
N(1)-Ni-N(2)	82.09(14)
N(5)-Ni-N(3)	96.33(12)
N(4)-Ni-N(3)	93.43(15)
N(1)-Ni-N(3)	93.67(15)
N(2)-Ni-N(3)	81.54(12)
N(5)-Ni-N(6)	76.98(11)
N(4)-Ni-N(6)	87.40(14)
N(1)-Ni-N(6)	87.43(13)
N(2)-Ni-N(6)	105.16(11)
N(3)-Ni-N(6)	173.30(12)

rings of bpy are coplanar with rms deviations of 0.005 and 0.012 $\text{\AA}$, respectively, and intersects at 7.91(16) $^\circ$. The

Fig. 2 Molecular structure along with the labeling atoms, excluding perchlorate ions and hydrogen atoms. Thermal ellipsoids are drawn at the 30% probability level.

tetradentate ligand consists of three five-membered chelate rings in *gauche* conformations, and in planar structures with a maximum rms deviation of 0.197 $\text{\AA}$. The *trans* bond angles, N(5)-Ni(1)-N(2), 177.82(12) $^\circ$, N(3)-Ni(1)-N(6) 173.30(12) $^\circ$ and *cis* bond angles, N(2)-Ni(1)-N(6), 105.16(11) $^\circ$ and N(5)-Ni(1)-N(3), 96.33(12) $^\circ$ are supported that N(2), N(3), N(5) and N(6) constitute an equatorial square base, with a planar rms deviation of 0.005 $\text{\AA}$, of the octahedron. Since all tren-N atoms do not face a similar environment, the chelate bite angles are so different. The Ni-N(tren) bond lengths of this complex are almost equivalent to the reported values of $[\text{Ni}_2(\text{tren})_2(\text{trien})](\text{ClO}_4)_4$, $[\text{Ni}(\text{tren})(\text{acetato})](\text{ClO}_4)_2$ and $[\text{Ni}_2(\text{tren})_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2$.²⁻⁴ The bond distances Ni(1)-N(5) and Ni(1)-N(6) are 2.075(3) and 2.196(3) $\text{\AA}$, respectively. Both are bidentate nitrogens, though the latter bond distance is longer than the former. This is due to the fact that N(6) is *cis*-oriented of sterically hindered tertiary tren nitrogen. The bond angle between the bpy nitrogens is 76.98(11) $^\circ$, which is comparable to the reported bond angles (79.0 $^\circ$) of the Ni(bpy)₃²⁺ complex.⁵ The two perchlorate ions have a disordered structure, as indicated by the splitting oxygen atoms of O12 and O24. All H-atoms were placed geometrically and refined as riding on their parent atoms with $U_{\text{iso}} = 1.2U_{\text{eq}}$ (N or C). The hydrogen bonds formed between tren and bpy, and between tren and perchlorate oxygen atoms helps to stabilize the crystal structure.

Acknowledgements

The authors thank the National Science Council, ROC, for support under grants NSC90-2113-M-007-030 and NSC90-2112-M-007-063.

References

1. N. H. David and R. W. Andrew, *J. Chem. Soc., Dalton Trans.*, **1993**, 1337.
2. R. D. Willett, *Acta Cryst.*, **1987**, C43, 1494.
3. H.-K. Fun, B.-C. Yip, Z.-L. Lu, C.-Y. Duan, Y.-P. Tian, and X.-Z. You, *Acta Cryst.*, **1996**, C52, 509.
4. I. Castro, M. L. Calatayud, J. Sletten, F. Lloret, and M. Julve, *J. Chem. Soc., Dalton Trans.*, **1997**, 811.
5. A. Wada, C. Katayama, and J. Tanaka, *Acta Cryst.*, **1976**, B32, 3194.