Inorganica Chimica Acta, 54 (1981) L243–L247
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Structure of a Diamagnetic Tetragonal Complex of Nickel: Tetrakis-(1-methylimidazoline-2(3H)-thione)nickel(II) Perchlorate

M. E. O'NEILL, E. S. RAPER

School of Chemical and Life Sciences, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne, NE1 8ST, U.K.

I. W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Sheffield, S1 1WB, U.K.

and J. A. DANIELS

ICI Corporate Laboratory, The Heath, Runcorn, Cheshire, WA7 4QE, U.K.

Received July 21, 1981

Introduction

Complexes of nickel(II) with S-donor ligands are renowned fro their versatility with respect to stereochemistry, visible-spectra, magnetic properties and structural equilibria in solution [1]. In particular, complexes of general formula, NiL_4X_2, exhibit all possibilities from effectively octahedral paramagnetic to square diamagnetic species [2–5]; some complexes also exhibit temperature dependent magnetic moments [6]. A particularly difficult structural distinction to make is that between extreme tetragonally distorted diamagnetic complexes and their square-planar counterparts; both types of complex have essentially similar electronic absorption spectra [7].

We have reported previously the complexes formed between 1-methylimidazoline-2-thione (MImt) and nickel(II) [3], of these, only the chloro and thiocyanato complexes are paramagnetic, the remainder are diamagnetic at room temperature. Infrared spectroscopy and electrolytic conductivity data supported the presence of ionic perchlorate in the solid and in solution for $Ni(MImt)_4(ClO_4)_2$. However, in view of the previously mentioned difficulties in distinguishing between square and tetragonal diamagnetic complexes and also because of the possibility of π-character in the Ni–S bonds we have undertaken the crystal structure analysis of $Ni(MImt)_4(ClO_4)_2$.

Results and Discussion

The intensity data for the triclinic crystal were collected on a Stoe Stadi-2 two-circle diffractometer using monochromated MoKα (λ = 0.71017 Å) radiation. Crystal data are summarised in Table I.

The structure was solved from 1922 unique non-zero ($I \leqslant 3\sigma(I)$) reflections. Non-hydrogen atom coordinates were obtained from Patterson and difference Fourier syntheses and were refined with anisotropic temperature factors by full matrix least squares methods to a final R = 0.0582. Positional parameters for the H-atoms were included in the calculations but not refined. Common isotropic temperature factors were applied to the olefinic, imido and methyl H-atoms respectively and refined to final values of U = 0.1390(265) $Å^{-2}$; 0.17623(357) $Å^{-2}$ and 0.2258(273) $Å^{-2}$. Methyl groups were refined as rigid groups.

Scattering factors for all atoms were calculated from analytical approximation (International Tables for X-ray crystallography [8]), SHELX and related programs were used in the analysis. Calculations were performed on the SRC, IBM 370/165 computer at Daresbury. Final fractional atomic coordinates are listed in Table II. Anisotropic thermal parameters, observed and calculated structure factors and equations of least squares planes have been deposited with the Editor.

The crystal structure of $Ni(MImt)_4(ClO_4)_2$ consists of tetrahedrally distorted square planar complexed cations and ionic perchlorates held together by a combination of H-bonds and Van der Waals forces. Bond lengths and angles are in Table III; a perspective view of the complex is in Fig. 1.

The Ni–S distances range from 2.213–2.242 Å and are shorter than the sum of their covalent radii (2.43 ± 0.1 Å) [9]. These contacts are more typical

TABLE I. Crystal Data.

a = 14.900(8)	b = 10.697(7)	c = 9.884(7) Å
α = 90.98(8)	β = 94.53(7)°	γ = 67.62(8)°
U = 1452.22 $Å^3$	D_c = 1.64 g cc^{-3}	D_m = 1.65 g cm^{-3}
Z = 2	F(000) = 732	μ = (MoKα) = 5.50 mm^{-1}
Space Group $P\bar{1}$		

TABLE II. Final Fractional Coordinates ($\times 10^4$) with e.s.d.s in Parentheses.

Atom	x	y	z
Ni	2471(1)	0617(1)	1999(2)
S1	1134(2)	0407(3)	2615(5)
C11	0985(9)	2010(15)	5236(20)
C21	1263(9)	−0099(15)	4345(22)
N11	1156(9)	0679(15)	5256(23)
N31	1436(9)	−1390(13)	4771(22)
C41	1414(14)	−1263(36)	6144(34)
C51	12(9)	0024(25)	6518(29)
S2	1593(2)	1743(3)	0142(4)
C12	−0633(8)	2129(16)	−0606(22)
C22	0561(6)	2874(8)	0732(13)
N12	−0368(5)	2987(8)	0346(12)
N32	0490(6)	3817(9)	1634(13)
C42	−0479(12)	4534(13)	1824(22)
C52	−1002(9)	4012(14)	1077(23)
S3	3872(2)	0436(3)	1240(4)
C13	3616(10)	3386(13)	0311(19)
C23	3659(6)	1150(10)	−0374(14)
N13	3569(6)	2396(9)	−0711(16)
N23	3566(6)	0544(11)	−1508(15)
C43	3406(9)	1433(21)	−2563(24)
C53	3404(9)	2619(17)	−2071(23)
S4	3351(2)	−0240(3)	3928(4)
C14	5183(10)	−2245(16)	5716(22)
C24	4064(7)	−1895(11)	3662(16)
N14	4813(6)	−2678(9)	4474(13)
N34	3978(6)	−2637(10)	2577(15)
C44	4710(9)	−3912(10)	2733(21)
C54	5216(9)	−3936(10)	3880(22)
Cl(1)	3359(2)	−2889(3)	−1167(5)
O1	3011(8)	−3735(9)	−1976(14)
O2	4185(12)	−3685(15)	−0446(23)
O3	2680(10)	−2001(17)	−0461(22)
O4	3658(13)	−2105(16)	−2007(22)
Cl(2)	1945(3)	−4983(4)	4063(7)
O5	2219(9)	−3855(18)	3350(25)
O6	1079(11)	−5823(19)	3799(27)
O7	2586(15)	−5689(19)	3918(31)
O8	2173(23)	−4675(32)	5312(31)
H111	0935	2388	6259
H112	0308	2540	4642
H113	1571	2170	4786
H31	1352	−2140	4106
H41	1676	−2130	6842
H51	1401	0310	7496
H121	−1416	2451	−0710
H122	−0313	1094	−0242
H123	−0374	2201	−1580
H32	1094	3928	2265
H42	−0741	5358	2507
H52	−1826	4455	0806
H131	3532	4321	−0183
H132	4312	2988	0893
H133	3041	3571	0979
H33	3695	−0532	−1643
H43	3376	1169	−3614
H53	3222	3561	−2630
H141	5789	−3092	6172
H142	4618	−1884	6412
H143	5423	−1444	5491
H34	3348	−2368	1855
H44	4797	−4726	2061
H54	5787	−4838	4429

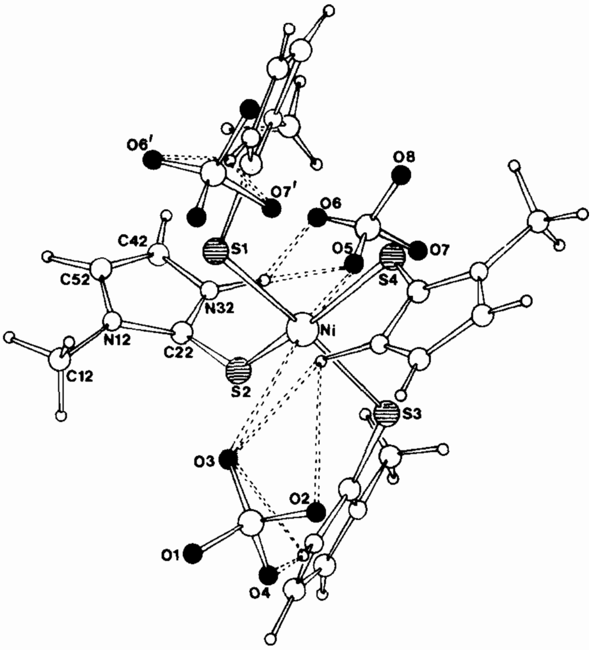

Fig. 1. Perspective view of the complex. Dotted lines represent the hydrogen bonding scheme and the Ni·····O interactions. Numbering scheme is shown in full for ligand 2, that for the remaining ligand is analogous.

of diamagnetic square-planar Ni(S–S)$_2$ chelates (2.15–2.24 Å) [10–14] than paramagnetic six-coordinate thiourea complexes (2.40–2.60 Å) [15–18] although MImt may be thought to be more closely related to the monodentate thiourea ligand.

The NiS_4^{2+} entity is distorted. Internal S–Ni–S angles range from 85.2 to 94.7°; S(1) and S(3) lie above the best mean plane through NiS$_4$, S(2) and S(4) lie below it; the deviations are virtually identical in each case and are in the range ±0.167–0.188 Å. Relatively short S····S non-bonded contacts (3.002–3.269 Å) are partially responsible for this 'tetrahedral' distortion. An additional factor is the methyl groups on the N(1) ligand atoms, three of which are '*syn*' with respect to the NiS$_4$ plane.

The range of Ni–S–C(2) angles (104.6–111.5°) suggest an essentially tetrahedral, sp^3, character for the thione S-atom such as has been observed in other MImt complexes [19–21].

TABLE III. Bond Lengths (A) and Angles (°) with e.s.d.s. in Parentheses.

Symmetry code; superscript: none *x*, *y*, *z*; (^{1}) *x*, −1.0 + *y*, *z*

(a) The coordination sphere

Bond Lengths	(A)	Bond Angles	(°)
Ni–S1	2.220(4)	S1–Ni–S2	88.0(1)
Ni–S2	2.242(4)	S1–Ni–S3	93.4(1)
Ni–S3	2.213(3)	S2–Ni–S4	169.2
Ni–S4	2.223(4)	S2–Ni–S3	172.4
S1···S2	3.101	S3–Ni–S4	85.2(1)
S2···S3	3.243	S4–Ni–S1	94.7(2)
S3···S4	3.002	Ni–S1–C21	111.5(5)
S4···S1	3.269	Ni–S2–C22	104.6(4)
Ni···O5	3.618	Ni–S3–C23	109.2(3)
Ni···O3	3.621	Ni–S4–C24	108.1(5)

(b) *Dimensions of the ligand molecules* (A = 1, 2, 3, 4)

Atoms	1	2	3	4	Average*
SA–C2A	1.776(22)	1.694(9)	1.734(14)	1.711(11)	1.713(11)
C2A–N3A	1.372(23)	1.314(16)	1.309(19)	1.350(20)	1.324(18)
N3A–C4A	1.364(40)	1.380(18)	1.368(27)	1.385(13)	1.377(23)
C4A–C5A	1.355(46)	1.300(26)	1.349(30)	1.306(27)	1.318(28)
C5A–N1A	1.411(36)	1.381(18)	1.356(27)	1.389(16)	1.375(20)
N1A–C2A	1.193(28)	1.366(12)	1.333(15)	1.327(14)	1.342(14)
N1A–C1A	1.349(22)	1.439(22)	1.468(21)	1.446(24)	1.451(22)
N3A–H3A	1.066(17)	1.097(11)	1.100(11)	1.082(11)	
C4A–H4A	1.092(34)	1.070(17)	1.075(23)	1.060(16)	
C5A–H5A	1.041(28)	1.146(12)	1.087(19)	1.127(13)	
SA–C2A–N3A	124.1(15)	127.2(8)	125.7(9)	126.3(9)	126.4(9)
N1A–C2A–N3A	113.2(21)	106.5(8)	106.8(13)	107.4(9)	106.9(10)
SA–C2A–N1A	122.7(15)	126.3(9)	127.5(11)	126.3(11)	126.7(10)
C2A–N3A–H3A	122.9(19)	126.2(8)	127.4(8)	124.9(8)	126.2(8)
H3A–N3A–C4A	131.4(23)	123.9(12)	123.6 (15)	125.2(12)	124.2(13)
C2A–N3A–C4A	102.6(21)	109.2(11)	108.4(14)	108.3(12)	108.6(13)
N3A–C4A–C5A	110.9(29)	108.7(14)	109.3(19)	107.7(13)	108.6(15)
H4A–C4A–C5A	124.4(30)	126.6(15)	126.3(22)	127.3(10)	126.7(16)
N3A–C4A–H4A	122.9(29)	124.7(16)	124.0(20)	124.9(15)	124.5(17)
C4A–C5A–H5A	124.6(26)	128.4(14)	127.5(21)	128.0(13)	128.0(16)
C4A–C5A–N1A	102.2(24)	107.0(12)	103.7(17)	108.1(10)	106.3(13)
H5A–C5A–N1A	130.6(25)	122.6(17)	128.5(18)	122.9(17)	124.7(17)
C5A–N1A–C1A	118.8(20)	125.9(10)	125.9(13)	126.3(11)	126.0(11)
C5A–N1A–C2A	111.0(18)	108.5(11)	111.9(13)	108.5(12)	109.6(12)
C2A–N1A–C4A	130.1(22)	125.5(9)	122.2(14)	125.0(10)	124.2(11)

*Averages apply to ligands 2, 3 and 4 only.

(c) *Dimensions of the perchlorate data*

Bond (A)			
Cl(1)–O1	1.412(13)	Cl(2)–O5	1.327(21)
Cl(1)–O2	1.354(17)	Cl(2)–O6	1.270(14)
Cl(1)–O3	1.330(17)	Cl(2)–O7	1.441(26)
Cl(1)–O4	1.400(22)	Cl(2)–O8	1.269(31)

(continued overleaf)

TABLE III. *(continued)*

Angle (°)			
O1–Cl(1)–O2	107.8(9)	O5–Cl(2)–O6	116.5(13)
O1–Cl(1)–O3	113.4(10)	O5–Cl(2)–O7	110.8(13)
O1–Cl(1)–O4	109.3(11)	O5–Cl(2)–O8	108.7(17)
O2–Cl(1)–O3	116.2(13)	O6–Cl(2)–O7	107.5(13)
O2–Cl(1)–O4	104.5(12)	O6–Cl(2)–O8	114.4(18)
O3–Cl(1)–O4	105.0(11)	O7–Cl(2)–O8	97.2(22)

(d) *H-bonded contacts*

Bond	(Å)
H31–O7^1	2.366
H31–O6^1	2.375
H32–O5	1.983
H32–O6	2.492
H33–O4	1.734
H33–O3	2.864
H34–O3	2.399
H34–O2	2.833

The dimensions of the four ligand molecules are essentially the same; the unusually large errors associated with ligand 1 were not responsive to librational correction although they probably result from an unusual degree of thermal perturbation of this ligand. The average C(2)–S distance (1.729 Å) possesses a SCF π-bond order of 40% [22].

The dihedral angles which result from the 'twisting' of the ligand molecules about the Ni–S–C(2) axes range from 13.6–84.2°. These values compare with the range 66.2–77.2° observed in tetrahedral Co(II) and Zn(II) complexes of the ligands [19–21]. Dihedral angles which result from the 'tilting' of the ligands relative to the NiS_4^{2+} plane range from 72.6–87.8°. These dihedral angles probably arise as a result of accommodating the sterically-hindered methyl groups and also in order to favourably orientate the imido (NH) groups for H-bonding with the perchlorate O-atoms.

Perchlorate groups occupy approximately axial positions relative to the NiS_4 plane and have long Ni–O distances of 3.618 and 3.621 Å. Pairs of O-atoms from the perchlorate groups are H-bonded to an imido H-atom in either a symmetrical (H31··· O6′, O7′) or an unsymmetrical (H32···O5, O6) manner.

The two features of this structure which particularly merit discussion are the short Ni–S distances and the axial positions of the perchlorate groups relative to the NiS_4^{2+} plane.

The former is indicative of significant π-character in the Ni–S bond and confirms the deduction previously drawn from the visible spectra of the Ni(II) complexes of MImt [3]. In addition, the room temperature diamagnetism of the complex is most likely a consequence of π-character in the Ni–S bonds and the enhanced ligand field strength which results from such an interaction. The balance between σ-donor and π-acceptor behaviour of the S-atoms results in a moderate positive charge on the central Ni(II) ion which is accommodated by relatively long contacts to the O-atoms (O3, O5) of the perchlorate groups [1, 5]. Consequently the complex is more properly described as tetragonal rather than square-planar and in this respect is similar to the diamagnetic $Ni(diars)_2I_2$ complex where apical Ni–I contacts of 3.20 Å have been observed [23].

Acknowledgement

One of us (I.W.N.) is grateful to the SRC for the provision of computing facilities and an equipment grant.

References

1 D. R. Eaton and K. Zaw, *Can. J. Chem., 53,* 633 (1975).
2 S. L. Holt and R. L. Carlin, *J. Am. Chem. Soc., 86,* 3017 (1964).
3 E. S. Raper, M. E. O'Neill and J. A. Daniels, *Inorg. Chim. Acta, 41,* 145 (1980).
4 Ibid., 41, 201 (1980).
5 *Ibid.,* in the press (1981).
6 S. L. Holt, R. J. Bouchard and R. L. Carlin, *J. Am. Chem. Soc., 86,* 579 (1964).

7 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, New York (1968).

8 'International Tables for X-ray Crystallography', (1974), Vol. IV, Table 2.2B. Birmingham, Kynoch Press.

9 L. Pauling, 'The Nature of the Chemical Bond', 3rd Ed. Cornell Univ. Press, (1960).

10 F. G. Gasparri, M. Nardelli and A. Villa, *Acta Cryst., 23,* 384 (1967).

11 M. Bonamico and G. Dessey, *Acta Cryst., 19,* 619 (1965).

12 M. Franzini, *Z. Krist., 393,* 118 (1963).

13 T. Sato, K. Nagata, M. Shiro and S. Koyama, *Chem. Comm.,* 192 (1966).

14 L. Cavalca, M. Nardelli and F. G. Gasparri, *Acta Cryst., 15,* 1139 (1962).

15 M. Nardelli, G. Gasparri, G. Battistini and P. Domiano, *Acta Cryst., 20,* 349 (1966).

16 A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.,* 1309 (1963).

17 H. Luth and M. R. Truter, *J. Chem. Soc. (A),* 1879 (1968).

18 W. T. Robinson, S. L. Holt and G. B. Carpenter, *Inorg. Chem., 6,* 605 (1967).

19 E. S. Raper and I. W. Nowell, *Acta Cryst., B35,* 1600 (1979).

20 A. G. Cox, I. W. Nowell and E. S. Raper, *Acta Cryst., B35,* 3047 (1979).

21 E. S. Raper and I. W. Nowell, *Inorg. Chim. Acta.*

22 N. Trinajstic, *Tetr. Letts., 12,* 1529 (1968).

23 C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.,* 4379 (1960).