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The Crystal Structure of Tetrakis(1-methylimidazoline-2(3H)-thione)di-bromo nickel(II): a Low-Spin Monodentate NiS_4 System

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Introduction

Complexes involving nickel(II) and 1-methylimidazoline-2(3H)-thione (*MImt*) of composition $Ni(MImt)_4X_2$ (X = Cl, Br, I. NO_3, ClO_4 or BF_4) or $Ni(MImt)_2(NCS)_2$ have been prepared [1]. The chloride and thiocyanate complexes are paramagnetic, the remainder are diamagnetic at room temperature. One of the major factors which is believed to govern electron distribution within coordinated nickel(II) species, such as those above, is the relative positions of both ligand and counter ion in the spectrochemical series. With closely related positions tetragonal paramagnetic complexes are likely and have been found for *MImt* with chloride and thiocyanate [1]. With significantly divergent positions the tetragonal component of the ligand field diminishes, relative to that of the equatorial ligands, and diamagnetic complexes are expected. Whether the resultant compounds are tetragonal or square in character is difficult to determine spectroscopically [2]. An X-ray study of $Ni(MImt)_4(ClO_4)_2$ [3] showed an essentially tetragonally distorted complex where a square environment was expected [1]. Accordingly we now report the crystal structure of $Ni(MImt)_2Br_4$ which, in view of the closer proximity of ligand and counter ion in the spectrochemical series, than occurs in the perchlorate complex, may reasonably be expected to be tetragonal rather than square. The ligand (*MImt*) is also expected to be monodentate S-donating on the basis of previously reported spectroscopic data [1] and by comparison with the established structure of the corresponding perchlorate complex [3].

Results and Discussion

The complex was prepared by a previously reported method and characterised by chemical analysis, thermal analysis and spectroscopic methods [1]. Relevant crystal data are listed in Table I; the intensity data were corrected for Lorentz, polarisation and absorption effects. The coordinates of the non-H atoms were determined by a combination of Patterson synthesis, direct methods and difference Fourier syntheses. These coordinates were then refined by means of full-matrix least squares methods with anisotropic temperature factors. Positional parameters of the H-atoms were included in the calculations but were not refined. Those of the imido (NH) groups were obtained by difference Fourier methods, the remainder were fixed by the program (C–H = 1.08 Å) with the methyl groups treated as rigid groups. Common isotropic temperature factors were applied and refined to the imido, olefinic and methyl H-atoms; final *U*-values (Å) are 0.093(38), 0.087(27) and 0.109(65) respectively. Scattering factors for all atoms were calculated from an analytical approximation [4]. Final atomic parameters are in Table II.

TABLE I. Crystallographic Data.

Compound	$NiC_{16}H_{24}N_8S_4Br_2$
Mr	675.2
a, Å	18.629(5)
b, Å	13.918(2)
c, Å	20.367(3)
$\alpha = \beta = \gamma$, deg	90
U, Å^3	5280.7
Z	8
D_c, Mg m^{-3}	1.68
D_m, Mg m^{-3}	1.66
Space group	Pbca
Radiation, Å	Mo, Kα, 0.71073
$F(000)$	2704
μ, cm^{-1}	39.80
Diffractometer	Enraf-Nonius CAD-4
Total data	3697
$I > 2\sigma(I)$	2250
R	0.0495
R_w	0.0538
w	$0.3728/[(\sigma)^2F_o + 0.009983(F_o)^2]$

All calculations were performed on the NUMAC, IBM 370/168 computer at the University of Newcastle upon Tyne. SHELX [5] and related programs were used in the determination of the crystal structure. [Anisotropic temperature factors, observed and calculated structure factors and structurally insignificant H-atom coordinates have been deposited with the Editor].

The crystal structure consists of distorted square planar complex cations, $[Ni(Mimt)_4]^{2+}$ and bromide ions held together by a combination of H-bonds and van der Waals' forces. Bonds lengths and angles are

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TABLE II. Final Fractional Coordinates ($\times 10^4$) for non-H Atoms with e.s.d. s in Parentheses and B_{eq} Values [19].

Atom	x	y	z	B_{eq} (Å^2)
Ni	2861(1)	2950(1)	1228(0)	2.26(4)
Br1	1498(1)	4360(1)	3720(1)	5.03(5)
Br2	4876(1)	215(1)	1156(0)	4.42(5)
N11	4770(3)	3804(5)	2065(3)	2.6(3)
C11	4582(6)	4829(7)	2034(5)	4.9(5)
C21	4555(4)	3144(6)	1634(4)	2.6(4)
S21	3981(1)	3303(2)	969(1)	3.1(1)
N31	4866(4)	2319(5)	1812(3)	2.7(3)
C41	5297(5)	2475(7)	2346(4)	3.2(4)
C51	5228(5)	3393(7)	2501(5)	3.6(4)
N12	2560(4)	1151(6)	2610(3)	3.5(4)
C12	2985(6)	605(8)	2137(5)	5.1(5)
C22	2573(4)	2110(6)	2685(4)	2.9(4)
S22	3117(1)	2928(2)	2291(1)	3.4(1)
N32	2106(4)	2317(5)	3169(3)	3.1(3)
C42	1800(5)	1485(8)	3399(5)	4.2(5)
C52	2088(6)	767(8)	3041(5)	3.1(5)
N13	1078(3)	1776(5)	457(3)	2.9(3)
C13	1440(6)	850(7)	564(6)	5.3(6)
C23	1200(4)	2566(6)	819(4)	2.6(4)
S23	1727(1)	2700(2)	1500(1)	4.1(1)
N33	789(4)	3248(5)	538(4)	3.3(3)
C43	414(5)	2871(8)	25(4)	4.0(5)
C53	605(5)	1976(8)	−35(5)	3.9(5)
N14	3516(4)	1975(6)	−475(4)	3.5(4)
C14	3362(7)	1111(8)	−102(6)	5.7(6)
C24	3231(4)	2851(7)	−356(4)	2.7(4)
S24	2562(1)	3174(2)	186(1)	3.4(1)
N34	3514(4)	3435(5)	−803(3)	3.2(3)
C44	3973(5)	2937(9)	−1213(4)	4.3(5)
C54	3980(5)	2039(9)	−1000(5)	4.5(5)

in Table III, equations of mean planes with dihedral angles are in Table IV, Fig. 1 contains a perspective view of the complex.

The Ni–S distances, (2.207(2) to 2.217(2) Å) are significantly shorter than the sum of their covalent radii (2.43 Å) [6]. These distances are similar to those previously reported for the corresponding perchlorate complex [3] and are more typical of bidentate (S–S) chelates (2.15 to 2.24 Å) [7–11] than monodentate S-donating (thiourea) molecules (2.40 to 2.60) [12–15]. Furthermore, the former complexes are invariably diamagnetic whereas the latter may be either paramagnetic or diamagnetic.

The $\mathrm{NiS_4}^{2+}$ entity is distorted. Internal S–Ni–S angles range from 87.7(1) to 91.9(1); *trans*-related S(21) and S(23) lie above the best mean plane through $\mathrm{NiS_4}$ and the corresponding S(22) and S(24) atoms lie below it (Table IV). The scale of the 'tetrahedral' distortion appears to be slightly less than that previously observed for the corresponding perchlorate complex but the factors responsible are essentially the same in both cases, namely, relatively short S····S non-bonded contacts (3.066–3.179 Å), which result from correspondingly short Ni–S contacts. In addition, the methyl groups from three of the *Mimt* molecules are arranged *'syn'* with respect to the $\mathrm{NiS_4}$ plane.

The Ni–S–C(2) angles (109.8 to 113.2(3)°) are in the upper end of the range which have been reported for other *Mimt* molecules in square environments (104.1 to 113.5°) [3, 16, 17]. The dimensions of the four ligand molecules are essentially the same with an average C(2)–S(2) distance of 1.724 Å compared with 1.685 Å in the free molecule [18]. This is

TABLE III. Bond Lengths (Å) and Angles (°) with e.s.d. s in Parentheses. Superscript: symmetry code; (none) x, y, z; (′) 0.5 − x, 0.5 + y, z; (″) 0.5 − x, 1 − y, −0.5 + z.

(a) *The coordination sphere*

Bond lengths	(Å)	Bond angles	(°)
Ni–S21	2.207(2)	S21–Ni–S22	91.9(1)
Ni–S22	2.215(2)	S22–Ni–S23	87.7(1)
Ni–S23	2.212(2)	S23–Ni–S24	91.2(1)
Ni–S24	2.217(2)	S24–Ni–S21	88.7(1)
S21····S22	3.179	Ni–S21–C21	111.5(3)
S22····S23	3.066	Ni–S22–C22	109.8(3)
S23····S24	3.164	Ni–S23–C23	111.3(3)
S24····S21	3.093	Ni–S24–C24	113.2(3)
Ni····Br1	6.004		
Ni····Br2	5.331		

(b) *Heterocyclic molecules*

	A = 1	A = 2	A = 3	A = 4
C(2A)–S(2A)	1.739(8)	1.722(9)	1.710(8)	1.725(8)
C(2A)–N(1A)	1.333(10)	1.344(12)	1.342(11)	1.352(12)
N(1A)–C(1A)	1.470(11)	1.460(13)	1.471(12)	1.450(14)
C(2A)–N(3A)	1.337(10)	1.347(10)	1.347(11)	1.330(11)

(continued on facing page)

TABLE III *(continued)*

	A = 1	A = 2	A = 3	A = 4
N(3A)–C(4A)	1.369(11)	1.372(13)	1.362(12)	1.382(13)
C(4A)–C(5A)	1.322(13)	1.349(15)	1.301(15)	1.324(18)
C(5A)–N(1A)	1.358(11)	1.353(13)	1.364(11)	1.377(12)
N(3A)–H(3A)	1.023(7)	1.111(7)	1.020(7)	1.211(7)
S(2A)–C(2A)–N(1A)	127.6(6)	127.9(6)	129.2(7)	129.4(7)
S(2A)–C(2A)–N(3A)	126.0(6)	125.5(7)	126.4(7)	124.4(7)
N(1A)–C(2A)–N(3A)	106.4(7)	106.5(7)	104.4(7)	105.8(7)
C(2A)–N(1A)–C(1A)	124.7(7)	125.6(8)	123.9(7)	125.1(8)
C(1A)–N(1A)–C(5A)	126.0(7)	125.1(8)	125.8(8)	125.8(9)
C(2A)–N(1A)–C(5A)	109.2(7)	109.3(8)	110.2(7)	109.1(8)
C(2A)–N(3A)–H(3A)	133.2(7)	127.7(7)	115.8(7)	123.9(7)
H(3A)–N(3A)–C(4A)	117.2(7)	108.6(7)	133.1(8)	125.4(7)
C(2A)–N(3A)–C(4A)	109.5(7)	109.8(8)	110.2(8)	110.7(8)
N(3A)–C(4A)–C(5A)	106.6(8)	106.0(9)	107.6(8)	106.3(8)
C(4A)–C(5A)–N(1A)	108.2(8)	108.5(9)	107.6(8)	108.1(10)

(c) *Hydrogen bonded contacts*

Bond	Lengths			Angle
Br···H–N	Br····N	Br···H	H–N	Br···H–N
Br(2)···H(31)–N(31)	3.218(2)	2.195(1)	1.023(7)	179.0(4)
Br(1)···H(32)–N(32)	3.260(2)	2.517(1)	1.111(7)	123.2(4)
Br(2')··H(33)–N(33)	3.258(2)	2.325(2)	1.020(7)	151.5(4)
Br(1")··H(34)–N(34)	3.218(2)	2.102(2)	1.211(7)	151.4(4)

TABLE IV. Equations of Least Squares Mean Planes Referred to Orthogonal Axes with Distances (Å) of Relevant Atoms from the Planes in Square Brackets.

Plane A NiS_4

$0.1651X - 0.9792Y - 0.1180Z + 3.5238 = 0$

[Ni 0.088(1); S21 0.014(3); S22 −0.058(3); S23 0.015-(3); S24 −0.058(3)]

Plane B Ni S21 C21

$0.1536X - 0.9487Y - 0.2763Z + 3.7678 = 0$

Plane C Ni S22 C22

$0.6788X - 0.7168Y - 0.1597Z - 0.2756 = 0$

Plane D Ni S23 C23

$-0.1663X + 0.9860Y - 0.0149Z - 3.1247 = 0$

Plane E Ni S24 C24

$-0.3697X - 0.9283Y - 0.0393Z + 5.8803 = 0$

Plane F Ligand 1

$0.7796X + 0.2014Y - 0.5930Z - 5.5311 = 0$

[N11 −0.031(6); C11 0.021(11); C21 −0.008(8); S21 0.006(2); N31 −0.002(7); C41 0.022(9); C51 −0.008-(10)]

Plane G Ligand 2

$-0.7228X + 0.1106Y - 0.6822Z + 6.9012 = 0$

[N12 0.005(7); C12 0.006(11); C22 0.031(8); S22 −0.028(2); N32 0.019(7); C42 −0.016(10); C52 −0.017(11)]

Plane H Ligand 3

$0.7564X + 0.2693Y - 0.5961Z - 1.6452 = 0$

[N13 −0.015(6); C13 0.018(11); C23 0.013(8); S23 −0.021(2); N33 0.031(8); C43 −0.016(9); C53 −0.010(10)]

TABLE IV *(continued)*

Plane I Ligand 4

$-0.7317X - 0.2279Y - 0.6424Z + 4.7911 = 0$

[N14 −0.007(8); C14 −0.011(13); C24 −0.052(8); S24 0.049(2); N34 −0.038(7); C44 0.031(9); C54 0.027(10)]

Dihedral angles

Planes	Angle (°)
A/F	89.91
A/G	98.46
A/H	93.92
A/I	79.74
B/F	84.69
C/G	117.45
D/H	81.46
E/I	59.51
F/H	4.11
G/I	19.63
F/G	97.86
H/I	103.41

consistent with a reduction of π-SCF character in the S–C bond from 52.0 to 37.0% upon coordination. The C(2)–N(1,3) distances are essentially unchanged upon coordination.

The dihedral angles (Table IV) which result from the '*twisting*' of the ligand molecules about the Ni–S–C(2) planes range from 59.5 to 117.4° and are closer to the values reported for tetrahedral (66.2–

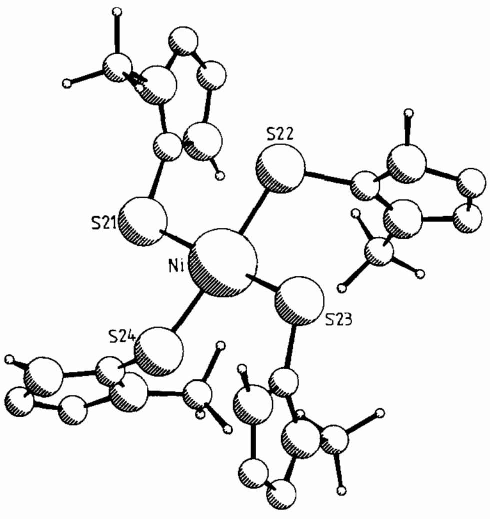

Fig. 1. Perspective view of the complex cation.

77.2°) than they are for square environments (13.6–84.2°) of previously reported *Mimt* complexes [18]. Dihedral angles resulting from '*tilting*' of the ligands relative to the NiS_4 plane range from 79.7 to 98.5°. This fairly narrow range is similar to the values reported for the corresponding perchlorate complex (72.6–87.8°) [3]. These dihedral angles result from a balance of several factors which include metal–ligand bonding, H-bonding (N–H····X) and the need to accommodate the sterically hindered methyl groups.

A significant feature of this structure is the fact that the bromide ions are effectively removed from the coordination sphere. Their function is to link neighbouring complex cations by means of N–H····Br···H–N contacts. All the resultant H-bonds appear to be strong (Table III(c)) as both the overall (Br····N) and (H····Br) distances are significantly shorter than the sum of their corresponding van der Waals' radii (Br = 1.95; H = 1.2; N = 1.5) [6]. Angles at the relevant hydrogen atoms are variable but that which involves H(31) is virtually linear.

The short Ni–S distances and diamagnetic character of this complex suggest that the position of *Mimt* in the spectrochemical series may be different from that which was deduced from the paramagnetic behaviour of the corresponding chloride and thiocyanate complexes [1]. The properties of this complex are more consistent with a ligand which possesses pronounced π-character and a position well to the right in the spectrochemical series. The factors which are normally involved in order to rationalise the balance between tetragonal and square geometries in complexes of type, NiL_4X_2, must be used with care when the ligand is a sulphur donor and the anion is capable of extensive H-bonding with the ligand. We suggest that the dominant factors in this instance are the π-character of the ligand and the H-bonding properties of the bromide ion.

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