The Phenomenon of Intramolecular Attractive S---O Interactions: Synthesis and Structure of (1,10-Phenanthroline)copper(II) Complexes with Isonitroso-(4-methylthiazol-2-yl)acetamide and Isonitroso-(4-methylthiazol-2-yl)-(benzothiazol-2-yl)methanide

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Isonitroso-(4-methylthiazol-2-yl)acetamide H(L¹), isonitroso-(4-methylthiazol-2-yl)(benzo-thiazol-2-yl)methanide H(L²) and their copper(II) complexes of composition [Cu(Phen){L¹}(ClO₄)] (1) and [Cu(Phen){L²}Cl]*C₂H₅OH (2) have been prepared. Crystal and molecular structures of the complexes have been determined from X-ray diffraction data (1: monoclinic, space group P2₁/c, with *a* = 11.611(2), *b* = 10.259(2), *c* = 17.869(4) Å, β = 104.67(3)°, V = 2059.1(7) Å³, Z = 4; R1 = 0.046 for the 2522 unique reflections with $I > 2\sigma(I)$. 2: triclinic, space group P1, with *a* = 8.351(1), *b* = 10.876(1), *c* = 14.891(2) Å, α = 96.170(8)°, β = 94.201(9)°, γ = 106.721(9)°, V = 1280.1(2) Å³, Z = 2; R1 = 0.034 for the 4038 unique reflections with $I > 2\sigma(I)$. In the structure of **1** the coordination polyhedron of Cu²⁺ is a distorted square pyramid with an oxygen atom of the ClO₄ counter anion in the apex (Cu-O 2.505(3) Å); in complex **2** the copper atom adopts fivefold coordination of a slightly distorted trigonal-bipyramidal geometry with a chlorine atom in the equatorial plane (Cu-Cl 2.3504(9) Å). Ethanol of crystallization gives rise to a hydrogen bond at the chlorine atom. In both structures the oximic anions are coordinated to the metal center in a bidentate chelate manner *via* the nitrogen atom of the nitroso group and the carbonyl oxygen atom (**1**) or *via* the benzothiazole nitrogen atom (**2**) (Cu-O, Cu-N in the range 1.963(2) - 2.031(2) Å). The thiazole group of the ligands takes no part in the coordination. The nitroso oxygen atoms possess short intramolecular contacts with thiazole sulphur atoms, with d(S---O) at 2.605(3) (1) and 2.676(3) Å (2), which may be attributed to a strong intraligand interaction.

Introduction

It is known, that in crystal structures sulphur atoms in aromatic group often manifest a "hypervalence" by forming short contacts with negative ions or with electronegative atoms [1]. Lately we have investigated the crystal structure of α -thiazolyloximes and their metal derivatives and have found that intramolecular attractive interactions of the S---O type strongly enforce a syn configuration of the nitrosogroup with respect to the thiazole sulphur atom (d \langle S---O \rangle 2.47 - 2.69 Å) [2 - 4]:



However, the factors affecting the stereochemistry of these compounds can often be more complicated, and it is difficult to predict the configuration of these species. A similar conclusion has been reached by Sax for thiamine derivatives [1]. In this context, α -thiazolyloximes have attracted attention as model compounds in thiazole chemistry and biochemistry, especially for the "special role" of sulphur atom in thiamine and althiomycin, a highly modified peptide antibiotic [1 - 2, 4 - 6]. In

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order to better characterize the phenomenon of the intramolecular attractive S---O interaction and its influence on the configuration of organic molecules complexed with metal ions, it was of interest to investigate the crystal structure of complexes of potentially ambidentate thiazolyloximes, including related molecules with two or more different types of sulphur atoms. In the course of these investigations we were successful in synthesizing new thiazolyloximes and coordination compounds thereof. Here we describe the preparation and results of X-ray investigation of copper(II) complexes containing the new ligands: isonitroso-(4-methythiazol-2-yl)-acetamide, $H(L^1)$, and isonitroso-(4-methylthiazol-2-yl)(benzothiazol-2-yl)-methanide, $H(L^2)$:



Experimental

Preparation of ligands

Bromoacetone was distilled twice and stored in a refrigerator prior to use. All experiments were carried out in air.

Isonitroso-(4-methylthiazol-2-yl)(benzothiazol-2-yl)methane (IV) was prepared by a three-step method according to the scheme:



The preparation of 2-cyanomethylbenzothiazole (I) was as described previously [7], and the synthesis of isonitroso-(4-methythiazol-2-yl)acetamide was carried out in a similar fashion starting with cyanoacetamide [3].

2-Benzothiazolylthioacetamide (II). To a hot solution of 10.4 g (60 mmol) of I in 100 ml of dry 2-propanol 2.0 g (37 mmol) of NaOCH₃ was added. The stirrer was

started and dry hydrogen sulphide was bubbled through the hot mixture (60°C) for 3 h. The resulting dark-brown solution was stored in a refrigerator (0°C) for 12 h, after which a slightly-yellow solid, 2-benzothiazolylthioacetamide, was filtered off and washed with 20 ml of cold 2-propanol and dried *in vacuo* over CaCl₂. Yield 11.0 g (89 %). m. p. 163°C. ¹H NMR spectrum (δ , ppm): 4.42 s (2H, CH₂), 7.48 m, 8.02 m (4H, CH), 9.81 s (2H, NH₂).

$C_9H_8N_2S_2$ (208.29)

Calcd C 51.89 H 3.87 N 13.45%,

Found C 52.10 H 3.77 N 13.36%.

(4-Methylthiazol-2-yl)(benzothiazol-2-yl)methane (III). To a suspension of 9.0 g (44 mmol) of II in 30 ml of 2propanol a solution of 8.0 g (58 mmol) of bromoacetone in 10 ml of 2-propanol was added dropwise over a 10 min period. The temperature was allowed to rise to about 40°C and the mixture was stirred for additional 2 h and left overnight. The orange-yellow precipitate, (III)*HBr, was collected, washed with 10 ml of 2-propanol and dried in air. Yield 11.5 g (81 %). ¹H NMR spectrum (δ , ppm): 2.38 s (3H, CH₃), 4.35 s (2H, CH₂), 7.35 s (1H, CH thiazole), 7.46 m, 8.05 m (4H, CH benzothiazole).

C₁₂H₁₀N₂S₂*HBr (327.26)

Calcd C 44.04 H 3.39 N 8.56%,

Found C 44.54 H 3.53 N 8.72%.

Isonitroso(4-methylthiazol-2-yl)(benzothiazol-2-yl)-

methane (**IV**). To a vigourously stirred suspension of 9.37 g (29 mmol) of (**III**)*HBr in 30 ml of 2-propanol and 50 ml of water 2.19 g (32 mmol) of solid NaNO₂ was added over a 20 min period at room temperature. The mixture was stirred for 5 h and the white precipitate filtered off, washed with 50 ml of water and dried *in vacuo* over H₂SO₄. After recrystallization from hot water, the yield was 7.06 g (89 %). ¹H NMR spectrum (δ , ppm): 2.47 s (3H, CH₃), 7.71 s (1H, CH thiazole), 7.45 m, 8.14 m (4H, CH benzothiazole), 14.04 s (1H, NOH).

C12H9N3OS2 (275.34)

Calcd C 52.34 H 3.29 N 15.26%, Found C 52.18 H 3.50 N 15.16%.

Preparation of coordination compounds

In order to characterize the bidentate coordination mode of the oximes prepared, coordination compounds of composition Cu(diamine) {L}X, where diamine = 2,2-dipyridyl, 1,10-phenanthroline were synthesized. A number of copper(II) oximates of similar stoichiometry have been reported earlier [8, 9].

Due to easy hydrolysis of the anionic oxime form $\{L^2\}^-$ to give $H(L^2)$, we were not successful in the preparation of analytically pure samples of alkali metal oximates, 2,2-dipyridyl or 1,10-phenanthroline and copper(II) salts CuX₂ (X = Cl, Br, ClO₄). A complex

	1	2		
Formula	C ₁₈ H ₁₄ ClCuN ₅ O ₆ S	C ₂₆ H ₂₂ ClCuN ₅ O ₂ S ₂		
Formula weight	527.4	599.6		
Crystal system	Monoclinic	Triclinic		
Space group	$P2_1/c$	P1		
Unit cell	a = 11.611(2), b = 10.259(2), c = 17.869(4),	a = 8.351(1), b = 10.876(1), c = 14.891(2),		
dimensions (A, °)	$\alpha = 90, \beta = 104.67(3), \gamma = 90$	$\alpha = 96.170(8), \beta = 94.201(9), \gamma = 106.721(9)$		
$V(A^3)$	2059.1(7)	1280.1(2)		
Z	4	2		
$D_{calc} (g \text{ cm}^{-3})$	1.70	1.56		
F(000)	1068	614		
$\mu (\mathrm{cm}^{-1})$	40.79	11.56		
Data collection				
T(K)	293	293		
Diffractometer	CAD-4 Enraf Nonius	STOE		
Radiation	CuKα	ΜοΚα		
Wavelength (Å)	1.54178	0.71069		
$2\theta_{\max}$ (°)	119.84	52.08		
Index ranges	$0 \le h \le 12, 0 \le k \le 11, -20 \le l \le 19$	$-10 \le h \le 10, -13 \le k \le 13, 0 \le l \le 18$		
Reflections collected	3223	5353		
Unique data	$3053 (R_{int} 0.033)$	$5068 (R_{int} 0.067)$		
Observed reflections	2522	4038		
Discrimination	2σ	2σ		
Structure refinement				
Data used	2869	4263		
Parameters refined	333	390		
Data to param. ratio	8.6	10.9		
R1 (obs.)	0.046	0.034		
wR2 (obs.)	0.125	0.093		
$GOF on F^2$	1.073	1.065		
Largest peak in the final	0.544	0.590		
difference map (e $Å^{-3}$)				

Table I. Experimental data for $[Cu(phen)\{L^1\}(ClO_4)]$ (1) and $[Cu(phen)\{L^2\}Cl]*C_2H_5OH$ (2).

Cu(phen){L}Cl*EtOH was prepared by direct synthesis in accordance with the general procedure described by Skopenko and Kokozay [10]. The following methods were used:

 $Cu(ClO_4)_2*6H_2O + (Phen*H_2O) + Na\{L^1\}$ = [Cu(Phen){L¹}(ClO_4)] + NaClO_4 + 7H_2O 2Cu + 2(Phen*HCl*H_2O) + 2H(L²) + 2EtOH + O_2 = 2[Cu(phen){L²}Cl]*EtOH + 4H_2O

Isonitroso-(4-methylthiazol-2-yl)acetamido-(1,10-phenanthroline)-copper(II) perchlorate (1)

To a hot solution of 0.370 g (2 mmol) of $H(L^1)$ in aqueous 2-propanol (1:1 v/v) (20 ml) 0.106 g (1 mmol) of Na₂CO₃ was added. The mixture was refluxed and stirred for 10 min and then added to the solution of 0.741 g (2 mmol) of Cu(ClO₄)₂*6H₂O and 0.396 g (2 mmol) of phenanthroline hydrate in aqueous 2-propanol (1:1 v/v) (20 ml). The resulting dark-green solution was heated to 70-80°C, quickly filtered and then cooled to room temperature during the period of 24 h. The dark-green prismatic crystals of the complex were filtered off and dried in air at room temperature. The yield was 0.760 g (72 %). The complex is soluble in hot water, aqueous 2-propanol and DMF.

 $\begin{array}{c} C_{18}H_{14}ClCuN_5O_6S~(527.39)\\ Calcd \ C~40.99 \ H~2.68 \ N~13.28 \ Cu~12.05\%,\\ Found \ C~40.22 \ H~2.81 \ N~13.02 \ Cu~11.75\%. \end{array}$

Isonitroso(4-methylthiazol-2-yl)(benzothiazol-2-yl) methanido-(1,10-phenanthroline)-copper(II) chloride, ethanol solvate (2)

Copper powder (0.0635 g, 1 mmol), 1,10-phenanthroline hydrochloride hydrate (0.2347 g, 1 mmol), $H(L^2)$ (0.2753 g, 1 mmol) and dry ethanol (40 ml) were placed in a flask; the mixture was stirred and refluxed for 2 h

Table II. Selected bond lengths (Å) and angles (°) for $[Cu(phen)\{L^1\}(ClO_4)]$ (1).

Cu-O(2)	1.963(2)	O(2)-C(2)	1.264(4)
Cu-N(1)	1.965(3)	N(2)-C(2)	1.312(5)
Cu-N(4)	2.009(3)	N(3)-C(3)	1.313(5)
Cu-N(5)	1.987(3)	N(3)-C(4)	1.373(4)
Cu-O(6)	2.505(3)	C(4)-C(5)	1.358(6)
C(1)-C(2)	1.467(4)	C(11)-C(12)	1.431(4)
C(1)-C(3)	1.437(5)	C(17)-C(18)	1.345(6)
S-C(3)	1.737(3)	Cl-O(3)	1.409(3)
S-C(5)	1.704(4)	Cl-O(4)	1.430(3)
O(1)-N(1)	1.292(4)	Cl-O(5)	1.420(3)
N(1)-C(1)	1.314(4)	Cl-O(6)	1.435(3)
O(2)-Cu-N(1)	81.7(1)	C(3)-S-C(5)	88.9(2)
O(2)-Cu-N(5)	95.4(1)	O(1)-N(1)-C(1)	119.2(3)
N(1)-Cu-N(4)	100.7(1)	N(1)-C(1)-C(2)	111.6(3)
N(1)-Cu-N(5)	176.8(1)	N(1)-C(1)-C(3)	123.0(3)
N(4)-Cu-N(5)	82.3(1)	C(1)-C(3)-N(3)	123.8(3)
N(1)-Cu-O(6)	91.1(1)	C(1)-C(2)-O(2)	119.1(3)
O(2)-Cu-O(6)	88.7(1)	C(3)-N(3)-C(4)	111.8(3)
Cu-O(6)-Cl	127.3(2)	N(3)-C(4)-C(5)	113.8(3)
C(1)-N(1)-Cu	114.5(2)	O(2)-C(2)-N(2)	122.1(3)
C(2)-O(2)-Cu	112.5(2)	H(1)-N(2)-H(2)	122(5)

untill total dissolution of copper was observed. To the cold mixture 5 ml of water was added and a small amount of a brown solid was filtered off. The clear, dark-green solution was allowed to stand at room temperature in a vacuum desiccator over H_2SO_4 for a few days, then dark-green crystals were collected and dried in air. Yield 0.324 g (54 %). The compound is soluble in ethanol, acetone, CHCl₃ and DMF and insoluble in water.

C₂₆H₂₂ClCuN₅O₂S₂ (599.60) Calcd C 52.08 H 3.70 N 11.68 Cu 10.60%, Found C 51.89 H 3.45 N 11.82 Cu 11.02%.

Measurements

¹H NMR spectra were recorded on a Bruker CXP-200 spectrometer (200.14 MHz) in DMSO-d₆ using tetram-ethylsilane as an internal standard.

For the X-ray diffraction study dark-green prismatic crystals of the dimensions $0.30 \times 0.27 \times 0.20$ mm (1) and $0.32 \times 0.27 \times 0.19$ mm (2) were used. Lattice parameters and the orientation matrix for data collection were obtained from least square refinement of the setting angles of 24 reflections with $12 < \theta < 15^{\circ}$. Semi-empirical absorption corrections based on ψ scans were applied. Table I lists details of cell parameters, data acquisition and structure refinement. The structures were solved by direct methods and subsequent Fourier difference techniques and refined by full-matrix least-squares techniques in the anisotropic approximation for all non-hydrogen atoms using SHELXS-86 and SHELXL-93 [11, 12]. The NH₂, OH and aromatic CH hydrogen atoms were located from

Table III. Selected bond length	s (A)	and	angles	(°)	for
$[Cu(phen){L2}Cl]*C_2H_5OH(2)$					

Cu-Cl	2.3504(9)	C(1)-C(3)	1.436(4)
Cu-N(1)	2.031(2)	C(2)-N(2)	1.321(4)
Cu-N(2)	1.994(2)	C(12)-N(2)	1.388(3)
Cu-N(4)	2.145(2)	C(3)-N(3)	1.309(4)
Cu-N(5)	2.002(2)	C(4)-N(3)	1.376(4)
S(1)-C(2)	1.724(3)	C(4)-C(5)	1.350(5)
S(1)-C(7)	1.736(3)	C(7)-C(8)	1.392(4)
S(2)-C(3)	1.730(3)	C(7)-C(12)	1.397(4)
S(2)-C(5)	1.711(4)	C(17)-C(18)	1.340(6)
N(1)-O(1)	1.281(3)	C(23)-C(24)	1.425(4)
C(1)-N(1)	1.330(3)	C(25)-O(2)	1.335(6)
C(1)-C(2)	1.443(4)	C(25)-C(26)	1.513(8)
N(2)-Cu-N(5)	172.1(1)	N(2)-C(2)-C(1)	119.4(2)
N(2)-Cu-N(1)	80.94(9)	C(2)-N(2)-C(12)	111.8(2)
N(5)-Cu-N(1)	93.7(1)	N(2)-C(2)-S(1)	115.2(2)
N(2)-Cu-N(4)	98.07(9)	N(3)-C(3)-S(2)	114.3(2)
N(5)-Cu-N(4)	79.90(9)	C(1)-C(3)-S(2)	123.8(2)
N(1)-Cu-N(4)	123.20(9)	C(5)-C(4)-N(3)	114.3(3)
N(1)-Cu-Cl	128.87(7)	C(4)-C(5)-S(2)	111.4(3)
N(2)-Cu-Cl	96.51(7)	C(2)-S(1)-C(7)	89.2(1)
N(4)-Cu-Cl	107.79(7)	C(5)-S(2)-C(3)	88.7(2)
N(5)-Cu-Cl	91.40(8)	N(1)-C(1)-C(3)	123.8(3)
C(1)-N(1)-Cu	114.3(2)	N(1)-C(1)-C(2)	113.0(2)
C(2)-N(2)-Cu	112.3(2)	C(3)-N(3)-C(4)	111.3(3)
O(1)-N(1)-C(1)	118.7(2)	N(2)-C(12)-C(7)	113.2(3)

the difference-Fourier syntheses and refined isotropically. The aliphatic CH₂ and CH₃ hydrogen atoms were placed at calculated positions with their isotropic U values set invariant at 0.08 Å². Refinements were terminated with all non-hydrogen parameter shifts $< 0.20 \sigma$; the weighting schemes were $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and *a* and *b* are constants adjusted by the program. Convergence was obtained at the values given in Table I. The principal interatomic distances and angles are listed in Tables II and III. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [13].

Results and Discussion

The molecular structure of

[Cu(Phen){ L^1 }(ClO₄)] (1) is presented in Fig. 1, which demonstrates a nearly square planar configuration at the copper atom with two phenanthroline nitrogen atoms (Cu-N(4) and Cu-N(5) at 2.009(3) and 1.987(3) Å, respectively) and nitrogen N(1) and oxygen O(2) atoms (Cu-N(1) at 1.965(3) Å and Cu-O(2) at 1.963(2) Å, Table II). The mean planes of the phenanthroline molecule and the group { L^1 } intersect at an angle of *ca.* 6.8(1)°, so that the structure of the fragment Cu(Phen){ L^1 } is actually planar.





Fig. 2. Fragment of the crystal structure of the $[Cu(phen)\{L^1\}(ClO_4)]$ complex (1).

In both five-membered chelate rings (Fig. 1) the angles about the copper atom, N(1)-Cu-O(2) and N(4)-Cu-N(5) of *ca.* 81.7(1) and 82.3(1)°, respectively, are typical for related systems [8, 9, 14]. The atoms of each metallocycle, CuN(1)C(1)C(2)O(2) and CuN(4)C(11)C(12)N(5), are practically coplanar (the maximum deviation from the least squares planes does not exceed 0.021(1) Å) and the copper atom resides exactly in the mean plane of atoms N(1), O(2), N(4), N(5). The [4+1] coordination environment of the copper is completed by the O(6)

oxygen atom of a perchlorate counter anion in the apex of a distorted square pyramid. The Cu-O(6) bond length is found to be 2.505(3) Å, which is typical for the weak Cu-O and Cu-F interactions in copper(II) perchlorate and tetrafluoroborate complexes with chelating ligands [14].

The complex units $[Cu(Phen){L^1}(ClO_4)]$ pack forming "dimers" (Fig. 2), in which the units are connected by Cu---O(1a) (2-x, -y, 1-z) interactions at 2.967(3) Å, and the bonds Cu-O(6) and Cu---O(1a) practically colinear. These dis-



tances are much longer than the usual values for hexacoordinated (4+2 or 4+1+1) copper(II) complexes of a distorted square bipyramidal geometry [14] and, indicate weak van der Waals interactions [14]. Thus, the geometry is similar to that found in complexes with isonitrosomalonodiamide [Cu(Dipy){ONC(CONH₂)₂}Cl]*H₂O [9] and isonitrosothiocyanoacetamide

[Cu(Dipy){ONC(CN)CSNH₂}Br]*2(1,4-Diox)[8]. Significant deviations of the copper atom from the base of the square pyramid towards the apical chlorine (0.258(3) Å [9]) or bromine (0.35(1) Å [8]) atoms suggest relatively strong interactions of Cu²⁺ with the apical ligands Cl or Br [14].

The shortest intermolecular contact in the structure (1), N(2)---O(5b) (2-x, 1-y, 1-z) at 3.105(5) Å (Fig. 2) possibly reflects very weak hydrogen bonding.

The molecular structure of

 $[Cu(Phen){L^2}Cl]*C_2H_5OH$ (2) and the atom numbering scheme are shown in Fig. 3. Only one close contact between neighbouring molecules has been detected, O(1)---C(21a) (-1+x, y, z) of 3.056(4) Å. This distance may also be attributed to a very weak intermolecular hydrogen bond [15].

The copper atom adopts five fold coordination of a slightly distorted trigonal-bipyramidal geometry with equatorial chlorine and nitrogen N(1), N(4) atoms and axial nitrogens N(2) and N(5) (Fig. 3). The copper atom deviates by 0.047(1) Å from the equatorial plane towards N(2). The structure differs essentially

Fig. 3. Perspective view, with 40% probability ellipsoids, of the [Cu(phen){ L^2 }Cl]*EtOH complex (2), showing the atom numbering scheme.

from that of $[Cu(Phen){L^1}(ClO_4)]$ (Fig. 1) and similarly composed copper(II) oximate compounds $[Cu(Dipy){ONC(CONH_2)_2}Cl]*H_2O$ and $[Cu(dipy){ONC(CN)CSNH_2}Br]*2(1,4-Diox)$ studied earlier [8, 9]. Unlike **2**, these species have a square-pyramidal (4+1) coordination geometry. Apparently, the Cu(phen){L²}Cl molecular configuration in this case is strongly affected by steric influences. Thus, the phenanthroline carbon atom C(13) has a short van der Waals contact with the nitroso oxygen atom, C(13)---O(1) 3.090(3) Å (Fig. 3).

The Cu-N(1) (2.031(2) Å), Cu-N(2) (1.994(2) Å) and Cu-N(5) (2.002(2) Å) separations are typical for pentacoordinated copper(II) complexes with nitrogen donor ligands [14, 16], the Cu-N(4) distance of 2.145(2) Å is slightly longer. The coordination around Cu²⁺ is completed by a chlorine atom at a distance of 2.3504(9) Å.

There are two five-membered chelate rings and the mean planes of phenanthroline and oximic ligand groups intersect at an angle of $54.7(1)^{\circ}$. In the metallocycles the angles N(2)-Cu-N(1) $80.94(9)^{\circ}$ and N(4)-Cu-N(5) 79.90(9)°, are consistent with the data for **1** (Table II) and the isonitrosomalonodiamide complex [9]. The hydroxyl hydrogen atom of the ethanol molecule forms a hydrogen bond with a chlorine atom (Fig. 3): Cl---H-O(2) 3.231(8) Å, d(Cl---H) 2.08(7) Å and the angle Cl---H-O(2) is *ca*. 169(5)°.

The configuration of the oximate anions $\{L^1\}$ and $\{L^2\}$ and the modes of their coordination are the most important observations in these structures. As

R ¹	\mathbf{R}^2	Compound	Configuration ^a	Separat SO	ions, Å C-C ^b	Ref.
4-Methylthiazol-2-yl	CN	H{X}	syn	2.701(6)	1.449(6)	[4]
		$Tl(18$ -crown-6) $\{X\}$	syn	2.69(1)	1.442(9)	[2]
		$Pb(18$ -crown-6) $\{X\}_2$	syn	2.69(1)	1.42(2)	[4]
		$Cs(18$ -crown-6) ₂ { $H(X)_2$ }	syn	2.78(2)	1.43(1)	[4]
Benzothiazol-2-yl	CN	$Tl(18$ -crown-6){ $H(X)_2$ }	anti		1.446(6)	[20]
•		$Cs{H(X)_2}*H_2O$	anti		1.443(8)	[21]
2-Pyridyl	CN	$H{X}$	anti		1.480(2)	[22]
2-Quinolyl	CN	HĮXĮ	anti		1.474(4)	[22]
- ·		$Cs{X}$	anti		1.459(4)	[21]
Δ^2 -Thiazolin-2-yl	CN	$Tl(18$ -crown-6){X}	anti		1.47(1)	[4]
Δ^2 -Thiazolin-2-yl	CONH ₂	Ni $\{H(X)_2\}(ClO_4)*3H_2O$	anti		1.485(2)	[19]
4-Methylthiazol-2-yl	$CONH_2$	$H{X}$	syn	2.633(2)	1.456(2)	[3]
		$[Ph_4As]{X}*4H_2O$	syn	2.477(2)	1.452(3)	[18]
		$Cu(Phen){X}(ClO_4)$	syn	2.605(3)	1.437(5)	This
4-Methylthiazol-2-yl	Benzothiazol-2-yl	$Cu(Phen){X}Cl*EtOH$	syn	2.676(3)	1.436(4)	paper

Table IV. Geometry of the 2-isonitrosoheteryl derivatives $H{ONC(R^1)(R^2)}$ ($H{X}$) in the crystal structures.

^a Configuration of the nitroso group with respect to the R¹ substitute; ^b bond lengths ONC-C[R¹].

in the isonitrosomalonodiamide derivatives [9, 17], the configuration of $\{L^1\}$ is such that the nitroso nitrogen N(1) and carbonyl oxygen O(2) atoms can chelate the metal atom in the ligand plane and an amide hydrogen atom gives rise to intramolecular hydrogen bond as shown (Fig. 1): N(2)---N(3) 2.756(5) Å, N(2)-H(1) 0.90(5) Å, H(1)---N(3) 2.02(5) Å, angle N(2)-H(1)---N(3) 138(4)°. However, unlike the symmetrical isonitrosomalonodiamide, in the present case two different possibilities for the ligand chelation are to be expected:



In the latter configuration steric hindrance may arise for the 4-methyl group (Fig. 1), however, the configurations of the non-coordinated oxime H{L¹} [3] and the anion in the tetraphenylarsonium salt [Ph₄As]{L¹}*4H₂O [18] are the same, suggesting an important role of intraligand interactions. This may be rationalized in terms of a strong attractive interaction between the nitroso oxygen and thiazole sulphur atoms: S^{δ +---O^{δ -} [1-4]. The separation S(1)---O(1) in compound **1** is found at 2.605(3) Å,} which is significantly less than the standard S---O van der Waals separation ($r(O\langle van der Waals \rangle)$ 1.5; $r(S\langle van der Waals \rangle)$ 1.85 Å [14]).

The value agrees with those of the {L¹} group and related 2-thiazolyloximes reported earlier [2 - 4, 18] (Table IV). It may be assumed, that the preferable configuration of isonitroso-(4-methylthiazol-2yl)(benzothiazol-2-yl)methanide [{L²}] is such that the nitroso oxygen atom can maintain an effective contact S^{δ +}---O^{δ -} with the thiazole sulphur atom, but not with the benzothiazole one. Therefore, despite the somewhat weaker donor properties of the benzothiazole nitrogen atom compared with thiazole [15], the following chelate coordination mode is expected,



as confirmed by the present study.

In **2** the ambidentate ligand $\{L^2\}$ is coordinated *via* the nitrogen atoms of nitroso [N(1)] and benzothiazole [N(2)] groups (Fig. 3). Unlike $\{L^1\}$ (Fig. 1), the steric hindrances on both alternative donor centers are nearly the same (C(6) in the α -position to N(3) and C(11)-to N(2)). For (2) the intraligand contact S(2)---O(1) is found to be *ca*. 2.676(3) Å.

The geometrical parameters of the oximate anions $\{L^1\}^-$ and $\{L^2\}^-$ allow a direct comparison with structural analogues reported earlier [3, 9, 17-19]. The anions are actually planar and suggest the considerable π -electron delocalization involving nitroso, thiazole and carbamoyl (benzothiazole in $\{L^2\}$) groups [17]. The dihedral angle between mean planes of thiazole ring and the exocyclic carbamoyloxime fragment in $\{L^1\}$ is $3.6(3)^\circ$. In the anion $\{L^2\}^-$ the corresponding dihedral angle between mean planes of the thiazole cycle and benzothiazolyloxime fragment is $5.0(2)^\circ$.

The carbon-carbon separations, C(1)-C(2) of 1.467(4) Å and C(1)-C(3) of 1.437(5) Å (1)

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and C(1)-C(2) of 1.443(4) Å and C(1)-C(3) of 1.436(4) Å (2) (Table II) are less than the standard $C(sp^2)$ - $C(sp^2)$ distance of 1.48 Å [14], reflecting the conjugation between the appropriate functional groups. The C(NO)-C(thiazole) as well as C(NO)-C(benzothiazole) bond lengths agree with the data reported earlier [ca. 1.44(1)-1.45(1)] A, Table IV] and in each case are slightly less than the similar parameters in the 2-pyridyl-, 2quinolyl and carbamoyloximes. Thus, the C(NO)-CONH₂ bond lengths in isonitrosocyanoacetamide HONC(CN)CONH₂ [H(X)] were found to be 1.494(7) Å for $H(X)*(18-crown-6)*H_2O$ [23]; 1.47(1), 1.474(9) Å for $Ph_6Te_3O_2\{X\}_2$ [24] and the appropriate parameters for isonitrosomalonodiamide in the copper(II) complex [9] are 1.469(2) and 1.486(2) A.

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