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SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF 2-METHYLTHIOSEMICARBAZIDE COPPER(II) NITRATE, $[Cu(2MeTSC)_2(NO_3)_2]$

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Abstract—The copper(II) complex of 2-methylthiosemicarbazide (2MeTSC) was obtained to evaluate the influence of the ^{2}N-substitution on the structure and properties of thiosemicarbazide complexes. The crystal and molecular structures of $[Cu(2MeTSC)_2(NO_3)_2]$ were determined by single crystal X-ray diffraction. The complex is monomeric hexa-coordinated with a strongly tetragonally elongated octahedral structure. Two 2MeTSC groups coordinate to the metal ion as bidentate ligands through the hydrazinic nitrogen and the sulphur atom, determining a nearly square planar coordination. The fifth and sixth positions are occupied by oxygen atoms from two NO_3^- anions, at a long distance from the metal [Cu—O = 2.864(3) Å]. The Cu—S [2.262(1) Å] and Cu—N(3) [1.992(3) Å] bond lengths are shorter than those observed in similar thiosemicarbazide copper(II) compounds, indicating a stronger bond. Another point of interest is the association of the complex units into a three-dimensional network through hydrogen bonding ($O_2NO \cdots H—N$).

There has been a continuous interest in copper compounds with nitrogen and sulphur donor ligands because of their importance to the understanding of the chemistry of copper enzymes, which have the metal coordinated to nitrogen and sulphur.[1] Thiosemicarbazides and thiosemicarbazones are particularly interesting, owing to their pharmacological activity.[2,3] The antitumour activities of thiosemicarbazones and their metal derivatives have been extensively studied. Data suggest that among essential metals, Cu^{II} complexes have the greatest activity.[3,4]

In general, thiosemicarbazides act as bidentate ligands coordinating to the metal ion through the sulphur and hydrazinic nitrogen atoms. In solution, thiosemicarbazides and thiosemicarbazones present a thione–thiol equilibrium, as shown in Fig. 1. This equilibrium is a very important feature in the chemistry of these compounds. If the acidic hydrogen on the ^{2}N is replaced by another group, then only the thione isomer is possible, and the influence of this group on the chemical and pharmacological

Fig. 1. Thione–thiol tautomerism in thiosemicarbazides.

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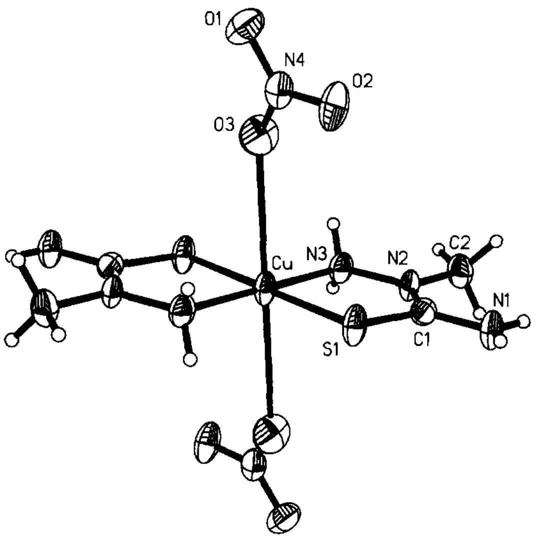

Fig. 2. ORTEP drawing of the $[Cu(2MeTSC)_2(NO_3)_2]$ molecule giving the numbering scheme for the atoms.

Table 1. Crystallographic data for $[Cu(2MeTSC)_2(NO_3)_2]$

Empirical formula	$CuC_4H_{14}N_8O_6S_2$
Formula weight	397.87
Crystal system	Monoclinic
Space group	$P21/c$
Unit cell dimensions	$a = 7.291(2)$ Å
	$b = 14.007(4)$ Å
	$c = 7.617(2)$ Å
	$\beta = 117.72(2)°$
Volume	688.5(3) Å^3
Z	2
$F(000)$	406
$2\theta_{max}$	110°
D_{calc}	1.92 g cm^{-3}

properties of the thiosemicarbazide and its derivatives can be evaluated.

Continuing our systematic studies on the chemistry of thiosemicarbazides and thiosemicarbazones,[5] we report here the synthesis and structural analysis of a copper(II) complex with 2-methylthiosemicarbazide (2MeTSC).

EXPERIMENTAL

All manipulations were performed under aerobic conditions. Copper(II) nitrate and 2-methylthiosemicarbazide (from Aldrich) were used as received. The title compound, $[Cu(2MeTSC)_2(NO_3)_2]$, was prepared by mixing ethanolic solutions of $[Cu(NO_3)_2]\cdot 2.5H_2O$ and 2MeTSC in a 1 : 2 molar ratio. Suitable crystals were obtained by slow evaporation of the solution.

Structure solution

A brown crystal with dimensions 0.08 × 0.32 × 0.10 mm was mounted in random orientation on a glass fibre; some experimental conditions are reported in Table 1. Data were collected on a Nic-

Table 2. Bond lengths (Å), angles (°) and hydrogen bonds in $[Cu(2MeTSC)_2(NO_3)_2]$

Cu—S	2.262(1)	Cu—N(3)	1.992(3)
S—C(1)	1.712(3)	C(1)—N(3)	1.320(5)
C(1)—N(2)	1.331(4)	N(2)—C(2)	1.457(5)
N(2)—N(3)	1.414(4)	N(4)—O(1)	1.243(4)
N(4)—O(2)	1.239(4)	N(4)—O(3)	1.246(3)
Cu—O(3)	2.864(3)		
S—Cu—N(3)	86.2(1)	Cu—S—C(1)	97.0(1)
S—C(1)—N(1)	118.5(3)	S—C(1)—N(2)	121.7(3)
N(1)—C(1)—N(2)	119.7(3)	C(1)—N(2)—C(2)	124.7(3)
C(1)—N(2)—N(3)	118.5(3)	C(2)—N(2)—N(3)	116.7(3)
Cu—N(3)—N(2)	116.4(2)	O(1)—N(4)—O(2)	120.2(3)
O(1)—N(4)—O(3)	119.5(3)	O(2)—N(4)—O(3)	120.3(3)

Bond D—H···A	Position of A	D—H	H···A	D···A	Angles (°) D—H···A
N(1)—H(1A)···O(2)	$-x, 1-y, -z$	0.88(4)	2.12(5)	2.954(4)	158(3)
N(1)—H(1B)···O(3)	$+x, 1+y, z$	0.80(5)	2.27(5)	2.992(4)	150(5)
N(3)—H(3A)···O(1)	$+x, 0.5-y, -0.5+z$	0.89(5)	2.07(6)	2.925(5)	161(4)
N(3)—H(3B)···O(1)	$1-x, 0.5+y, 0.5-z$	0.76(4)	2.39(4)	3.074(3)	152(3)
N(3)—H(3B)···O(2)	$1-x, 0.5+y, 0.5-z$	0.76(4)	2.39(4)	3.085(3)	154(3)

olet R3 four circle diffractometer, using Ni-filtered Cu-K_α radiation (1.54178 Å) at *ca* 293 K. Lattice parameters were obtained from 17 reflections with $12.63 < 2\theta < 26.68°$. A number of the 864 independent reflections were collected using the θ–2θ scan mode in the $3.0 < 2\theta < 110°$ range, and variable scan speed. The crystal stability was monitored using two standard reflections; no significant variations were observed. The final refinement of structural parameters used 786 reflections which had values of $F > 3\sigma(F)$.

The structure was solved by the heavy atom method incorporated into the SHEXTL system,[6] and refined by a least-squares technique with anisotropic temperature factors for the non-hydrogen atoms. The hydrogen atoms in the CH$_3$ group were allowed to ride on bonded carbon. Hydrogen atoms attached to nitrogen were found on the difference Fourier map at an advanced stage of anisotropic refinement, and their coordinates were refined. All hydrogen atoms were assigned fixed isotropic temperature factor, $U = 0.06$ Å^2. The minimized function was $\Sigma\ w\ (\Delta F)^2$, $w = [\sigma^2(F_0)+g(F_0)^2]^{-1}$, with final $g = 0.002$. The residual electron density was within -0.53 and 0.37 e A^{-3}; final $R = 0.0361$, $R = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$ and $R_w = 0.060$, $R_w = \{\Sigma[w^{1/2}(|F_0|-|F_c|)]/\Sigma\ w^{1/2}|F_0|\}$. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Supplementary data have been deposited with the Editor.

RESULTS AND DISCUSSION

The shape of the molecule and the atomic numbering are indicated in Fig. 2. Final atomic parameters are given in Table 1 and bond distances and angles in Table 2.

The molecule is centrosymmetric. The two 2MeTSC groups coordinate as bidentate ligands to the metal ion, through the sulphur and hydrazinic nitrogen atom. The Cu—S bond length is 2.262(1) Å, and the Cu—N(3) distance is 1.992(3) Å. The [Cu—S(1)—N(3)—S(1a)—N(3a)] coordination plane is symmetry restricted planar, with C(1) and N(2) both lying 0.083(3) Å above the plane; N(1) and C(2) are also 0.169(3) and 0.091(3) Å, respectively, above the plane. The mean plane deviation of the chelate rings Cu—N(3)—N(2)—C(1)—S(1) is 0.020 Å, with N(3) showing the maximum deviation, 0.0537 Å. The square planar coordination of the 2MeTSC ligands is complemented by two oxygen atoms from two nitrate groups at a long distance of 2.864 (3) Å, giving a strongly tetragonally elongated octahedral structure.

It seems that thiosemicarbazones tend to promote square planar coordination in Ni$^{\mathrm{II}}$[7] and Cu$^{\mathrm{II}}$[8]

Table 3. Comparison of bond lengths (Å) and angles (°) in thiosemicarbazide complexes

Compound	^{3}N—^{2}N	^{2}N—^{1}C	^{1}C—S	^{1}C—^{1}N	M—S	M—^{3}N	Ref.	^{3}N—M—S	M—^{3}N—^{2}N	M—S—^{1}C	^{1}C—^{2}N—^{3}N	Ref.
[Ni(2MeTSC)](NO$_3$)$_2$]	1.427(5)	1.315(5)	1.719(4)	1.315(5)	2.177(1)	1.896(3)	1	87.9(1)	117.0(2)	97.4(1)	116.0(3)	1
[Cu(2MeTSC)(NO$_3$)$_2$]	1.414(4)	1.331(4)	1.712(3)	1.320(5)	2.262(1)	1.992(3)	This work	86.2(1)	116.4(2)	97.0(1)	118.5(3)	This work
[Cu(HTSC)$_2$(NO$_3$)$_2$]	1.411	1.330	1.713	1.315	2.286	2.001	11	86.2				10
[Cu(HTSC)Cl$_2$]	1.407(5)	1.326(4)	1.717(4)	1.311(6)	2.266(1)	2.002(4)	12	86.2(1)	115.5(2)	97.2(1)	120.1(3)	11

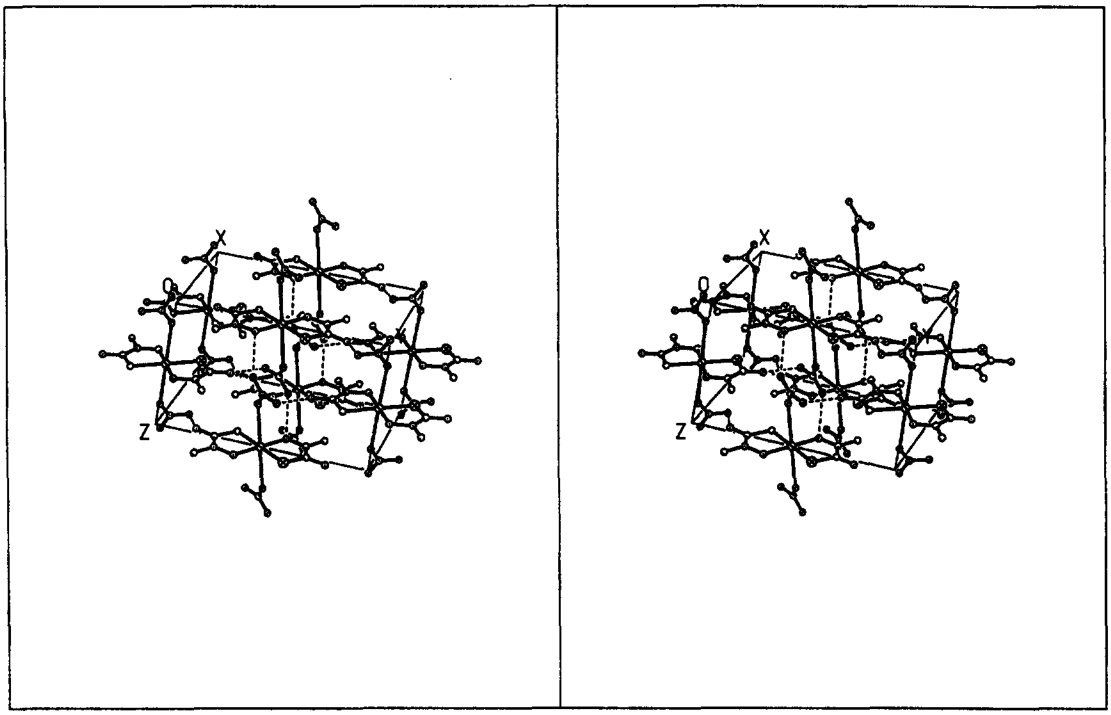

Fig. 3. Stereoscopic view of the crystal packing of $[Cu(2MeTSC)_2(NO_3)_2]$.

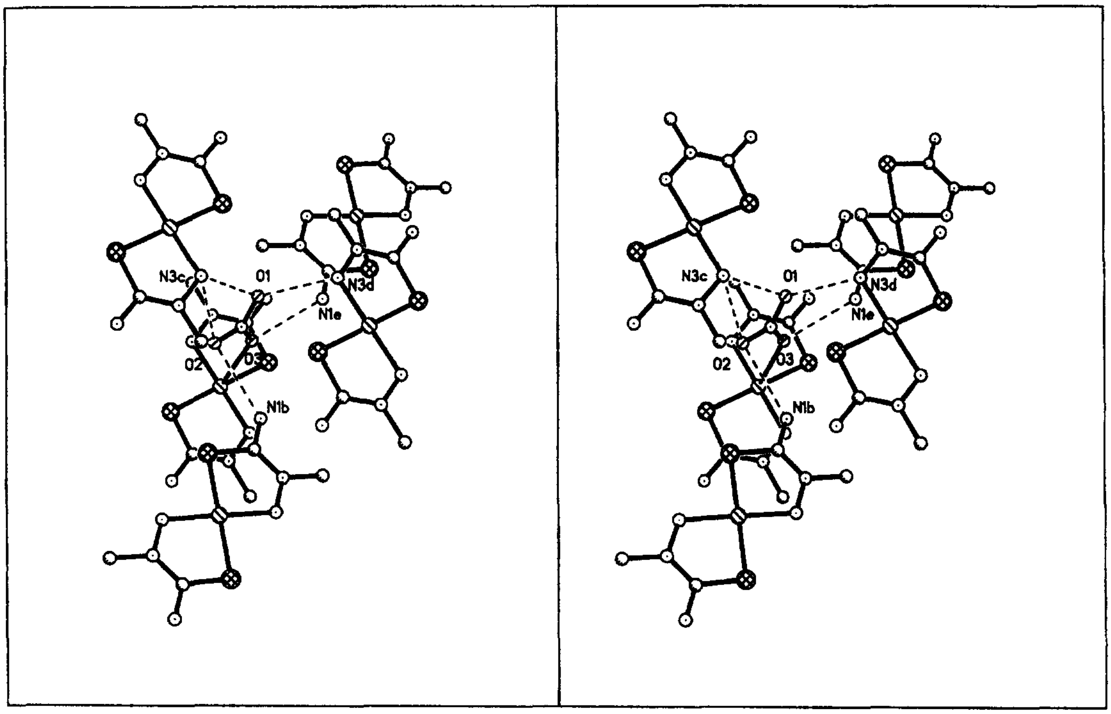

Fig. 4. Stereoscopic view of the hydrogen bond connection between the NO_3^- groups and the N(1) and N(3) atoms.

compounds. When the structure of $[Ni(2MeTSC)](NO_3)_2$[5] is compared with $[Cu(2MeTSC)_2(NO_3)_2]$, the first point to note is the difference in the coordination number. This difference reflects the higher tendency of Ni^{II} to be in a square planar environment. Although a 4+2 coordination in Cu^{II} compounds is common, it is interesting that the Cu—O bond length in this compound is longer that the usual Cu—O bond distances in octahedral Cu^{II} nitrate complexes (2.285 Å).[9] This bond distance is in the range of upper values for a long coordination distance (2.5–3.0 Å)[10] in Cu^{II} compounds.

The distances and angles in the Cu—N(3)—N(2)—C(1)—S(1) chelate ring suggest a greater delocalization in the Cu^{II} compound compared with the analogous Ni^{II} compound (Table 3). The Cu—S and Cu—N(3) bond lengths in $[Cu(2MeTSC)_2(NO_3)_2]$ are shorter than the ones observed in other Cu^{II} TSC compounds. This result suggests that the inductive effect of the methyl group in 2MeTSC builds a stronger bond between the Cu^{II} ion and the ligand.

The unit cell packing of the molecules is shown in Fig. 3. The copper(II) atoms are located at the middle of each cell edge. An interesting feature is the hydrogen bond interaction between the NO_3^- groups and the N(1) and N(3) atoms of the coordinated ligand (Figs 3 and 4). The hydrogen bonds create a supramolecular network, which stabilizes the crystal structure.

It is necessary to study the structure of more thiosemicarbazide and thiosemicarbazone copper compounds to evaluate the tendency to promote square planar coordination. The control of the geometry around a metal ion is important as a tool for controlling the properties of a compound. In the case of thiosemicarbazones, it may also be related to the pharmaceutical properties of these compounds.

Considering these results and the pharmacological activity shown by tridentate thiosemicarbazones, it is interesting to study the effect of substituents on ^2N upon the structure and properties of their Cu^{II} compounds. Work along these lines is in progress in our laboratory.

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REFERENCES

1. T. G. Spiro (Ed.), *Metal Ions in Proteins*. Wiley, New York (1981); J. Peisach, W. E. Blumberg and P. Aisen (Eds), *The Chemistry of Copper*. Academic Press, New York (1966).
2. S. Padhye and G. B. Kauffman, *Coord. Chem. Rev.* 1985, **63**, 127.
3. D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar and R. G. Yerande, *Coord. Chem. Rev.* 1993, **123**, 49.
4. H. G. Petering, H. H. Burskirk and J. A. Crim, *Cancer Res.* 1967, **27**, 1115.
5. J. Valdés-Martínez, R. A. Toscano and R. Cea-Olivares, *Acta Cryst.* 1991, **C47**, 2666.
6. G. M. Sheldrick, SHELEXTL-PLUS PC Version. Solution and Refining Package. Siemens Analytical X-Ray Inst. Inc. (1990).
7. M. Soriano-García, R. A. Toscano, J. Valdés-Martínez and J. M. Fernandez, *Acta Cryst.* 1985, **C41**, 498; J. Valdés-Martínez, R. A. Toscano, M. Soriano-García, M. Rubio, J. Gómez-Lara, M. A. Vázquez-M. and S. Carranza, *Polyhedron* 1989, **8**, 727; D. X. West, J. P. Scivill, J. V. Silverton and A. Bovoso, *Transiton Met. Chem.* 1986, **11**, 123; D. X. West, H. Gebremedhim, R. J. Butcher, J. P. Jasinski and A. E. Liberta, *Polyhedron* 1993, **18**, 2489.
8. R. J. Butcher and D. X. West, *Transition Met. Chem.* 1993, **18**, 449; J. Valdés-Martínez and R. A. Toscano, unpublished results.
9. A. Guy Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.* 1989, S1.
10. B. J. Hathaway, *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson), Vol. 5, Ch. 53 (1987).
11. M. J. M. Campbell, *Coord. Chem. Rev.* 1975, **15**, 279; from A. Ch. Villa, A. G. Manfredotti and C. Guastini, *Cryst. Struct. Commun.* 1972, **1**, 207; e.s.d. values not included.
12. D. Chattopadhyay, S. K. Majumdar, P. Lowe, C. H. Schwalbe, S. K. Chattophadyay and S. Ghosh, *J. Chem. Soc., Dalton Trans.* 1991, 2121.