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Transition Metal Complexes with Thiosemicarbazide-Based Ligands, IV: Synthesis and Molecular Structure of 5-Nitrosalicylaldehyde S-Methylisothiosemicarbazonato-piperidine-copper(II)

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Summary. The reaction of warm *DMF* solutions of Cu(II) perchlorate, 5-nitrosalicylaldehyde S-methylisothiosemicarbazone (H_2L) and piperidine (*Pip*) yielded the paramagnetic ($\mu_{eff} = 2.19$ B.M.) Cu(*L*)*Pip* complex, where *L* is the dianionic form of H_2L, formed as a result of deprotonation of the phenolic hydroxyl and NH_2 group. Crystal data of the complex are: monoclinic $P2_1$, $a = 11.902(4)$, $b = 6.765(3)$, $c = 11.343(4)$ Å; $\beta = 112.92°$, $V = 841.20(8)$ Å^3, $M = 400.9$, $Z = 2$, $d_0 = 1.60$ gcm^{-3}, $d_c = 1.58$ gcm^{-3}, $F(000) = 424$. The structure was refined to a residual $R = 0.047$. The copper(II) ion is coordinated in a square-planar arrangement by the piperidine nitrogen and the NNO set of donor atoms of *L*.

Keywords. Synthesis; Molecular structure; Infrared spectra; Magnetic moment; 5-Nitrosalicylaldehyde S-methylisothiosemicarbazonato-piperidine-copper(II).

Komplexe der Übergangsmetalle mit Thiosemicarbazid-Liganden, IV. Synthese und molekulare Struktur von 5-Nitrosalicylaldehyd-S-methylisothiosemicarbazonato-piperidin-kupfer(II)

Zusammenfassung. Durch die Reaktion in warmen *DMF*-Lösungen von Cu(II) Perchlorat, 5-Nitrosalicylaldehyd-S-methylisothiosemicarbazon (H_2L) und Piperidin (*Pip*) wurde ein paramagnetischer Komplex ($\mu_{eff} = 2.19$ B.M.) Cu(*L*)*Pip* erhalten, wobei *L* nach doppelter Deprotonierung (NH_2- und Phenolhydroxyl-Gruppe) als dianionische Form von H_2L vorliegt. Die kristallographischen Daten des Komplexes sind: monokline Raumgruppe $P2_1$, $a = 11.902(4)$, $b = 6.765(3)$, $c = 11.343(4)$ Å, $\beta = 112.92°$; $V = 841.20$ Å^3, $M = 400.9$, $Z = 2$, $d_0 = 1.60$ gcm^{-3}, $d_c = 1.58$ gcm^{-3}, $F(000) = 424$. Die Struktur wurde bis zu einem *R*-Wert von 0.047 verfeinert. Die Koordination des Kupfers wird quadratisch-planar über den Piperidin-Stickstoff und die NNO-Donorhülle der Chelatliganden gebildet.

Introduction

It has been shown [1, 2] that the terdentate NNO ligands based on nonsubstituted and substituted salicylaldehyde S-methylisothiosemicarbazone form with Cu(II) different mono(ligand) complexes of either normal (1.80–1.90 B.M.), or lower (1.0–1.6 B.M.) values of effective magnetic moment if compared to the spin-only value for the S = 1/2 system. The lower μ_{eff} values have been explained in terms of formation of dimeric (i.e. polymeric) complexes *via* the bridging atom, either the oxygen of the deprotonated phenolic hydroxyl, or the nitrogen of the S-methylthioamide group of the chelate ligand involved.

This work describes the synthesis, molecular and crystal structure of the complex Cu(*L*)*Pip* (*L* = dianion of 5-nitrosalicylaldehyde S-methylisothiosemicarbazone; *Pip* = piperidine) having the μ_{eff} of 2.19 B.M., a value which is higher than for other known Cu(II) complexes with similar ligands.

Experimental

The mixture of 0.50 g (2 mmol) of 5-nitrosalicylaldehyde S-methylisothiosemicarbazone, obtained by a procedure analogous to that already described [3] and 0.70 g (2 mmol) of $Cu(ClO_4)_2 6H_2O$ was dissolved by heating in 5 cm^3 of dimethylformamide (*DMF*). After adding 0.8 cm^3 of piperidine, the solution was left to evaporate slowly at room temperature for 50 h. The dark crystals were filtered off and washed throughly with *Et*OH and Et_2O. Yield: 0.40 g. Calculated for $CuC_{14}H_{19}N_5O_3S$ ($M = 400.89$): Cu 15.85, C 41.49, H 4.78, N 17.46. Found: Cu 15.67, C 42.32, H 5.01, N 17.35%.

Crystal data of the complex are: $CuC_{14}H_{19}N_5O_3S$, monoclinic $P2_1$, $a = 11.902(4)$, $b = 6.765(3)$, $c = 11.343(4)$ Å, $\beta = 112.92$, $V = 841.20(8)$ Å^3, $M = 400.8$, $Z = 2$, $d_0 = 1.62$ gcm^{-3}, $d_c = 1.61$ gcm^{-3}, $F(000) = 424$, μ(MoKα) = 14.09 cm^{-1}. Three-dimensional intensity data and accurate cell dimensions were measured on a four-cycle automatic diffractometer Philips PW 1100 using MoKα radiation. Of the 1336 unique reflections recorded with $2\theta < 50°$, 1274 with $I > 3\sigma(I)$ were used in the analysis. No absorption or extinction correction was applied.

The structure was solved by the heavy-atom method using three-dimensional Patterson and Fourier syntheses, and refined by least-squares methods using the program system Shelx-76 [4]. Anisotropic temperature factors were assumed for all non H-atoms and isotropic ones for hydrogen atoms. The hydrogen atoms belonging to the chelate ligand were found from difference Fourier map, the positions of remaining H atoms (from the piperidine ring) were calculated; CH-tetrahedral geometry and constrained C−H distance of 1.08 Å. Maximal residual density in the DF map was 0.60 e/Å^3, min. −0.42 e/Å^3. The least-squares refinement converged to a final $R = 0.047$. All atoms are located in two-fold general positions. The origin was defined by fixing the y/b fractional coordinate for copper atom to the zero value. Atomic scattering factors for copper including the correction for anomalous dispersion were taken from International Tables for X-ray Crystallography [5] other scattering factors as in Shelx-76. The anisotropic thermal parameters and list of F_0/F_c values are available on request from the authors.

Results and Discussion

Crystal Structure

Table 1 lists fractional atomic coordinates, whereas bond distances and angles are given in Table 2. The crystal structure consists of complex molecules containing Cu(II) as the central atom, the tridentate (NNO) chelate ligand in its twice deprotonated form as well as one molecule of piperidine. An approximately square-planar coordination (maximal deviation from best-plane 0.057 Å) around the Cu atom is formed by both two nitrogens and the oxygen atom of the chelate ligand and one nitrogen atom of the piperidine molecule. The displacement of the copper from this plane does not exceed 0.095 Å. The symmetry related chelate ligands from different molecules are approximatively situated in both $(x, 0, z)$ and $(x, 1/2, z)$ layers while the basal planes of the piperidine rings are almost perpendicular to them (Fig. 1).

Table 1. Fractional coordinates (× 10^4) for Cu(*L*)*Pip*

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	1 944 (1)	0	4 271 (1)	C(9)	9 343 (6)	101 (35)	3 596 (7)
S	5 101 (2)	55 (23)	7 926 (2)	C(10)	1 985 (20)	1 643 (32)	1 943 (22)
O(1)	243 (4)	−37 (37)	3 222 (4)	C(11)	1 900 (13)	1 788 (29)	595 (17)
O(2)	5 193 (5)	−230 (34)	3 616 (6)	C(12)	1 597 (8)	−216 (40)	−114 (8)
O(3)	6 336 (5)	−267 (28)	5 622 (6)	C(13)	2 274 (16)	−1 855 (33)	729 (18)
N(1)	3 592 (5)	−98 (43)	5 479 (6)	C(14)	1 758 (16)	−1 890 (26)	1 869 (13)
N(2)	2 703 (5)	−12 (37)	6 977 (5)	H(N1)	4 226 (51)	−9 (73)	5 369 (52)
N(3)	1 656 (5)	−134 (33)	5 841 (5)	H(N4)	3 272 (5)	−333 (39)	2 933 (6)
N(4)	2 303 (5)	−130 (39)	2 657 (6)	H(21)	4 216 (54)	−466 (70)	9 326 (57)
N(5)	6 201 (6)	−68 (38)	4 497 (6)	H(22)	4 259 (57)	1 540 (68)	9 117 (59)
C(1)	3 663 (6)	−28 (42)	6 660 (7)	H(23)	5 472 (54)	902 (66)	54 (58)
C(2)	4 745 (9)	360 (26)	9 290 (9)	H(3)	651 (47)	−72 (73)	6 837 (50)
C(3)	624 (6)	38 (44)	5 964 (6)	H(5)	8 551 (8)	−56 (73)	6 067 (51)
C(4)	9 461 (6)	3 (41)	4 883 (6)	H(7)	6 265 (52)	361 (69)	2 238 (52)
C(5)	8 414 (6)	−146 (37)	5 163 (6)	H(8)	8 161 (51)	474 (67)	1 783 (53)
C(6)	7 276 (6)	−53 (44)	4 181 (7)	H(101)	1 086 (20)	2 000 (34)	1 901 (22)
C(7)	7 131 (6)	63 (42)	2 915 (7)	H(102)	2 625 (20)	2 756 (34)	2 493 (22)
C(8)	8 141 (7)	124 (37)	2 634 (7)	H(111)	1 193 (13)	2 821 (29)	60 (17)
				H(112)	2 768 (13)	2 309 (29)	624 (17)
				H(121)	1 797 (8)	−131 (40)	−963 (8)
				H(122)	640 (8)	534 (40)	382 (8)
				H(131)	2 089 (16)	−3 236 (33)	211 (18)
				H(132)	3 240 (16)	1 550 (33)	1 092 (18)
				H(141)	2 034 (16)	−3 228 (26)	2 427 (13)
				H(142)	775 (16)	−1 774 (26)	1 483 (13)

The interatomic distances and angles within the chelate ligand of the title compound are in good agreement with the corresponding values found for a similar chelate ligand with the structure of Cu(*L*)*Im*H where *L* is the dianion of salicylaldehyde S-methylisothiosemicarbazone and *Im*H is imidazole [6].

The bond distances and bond angles in the S-methylisothiosemicarbazide fragment indicate a high degree of delocalization of π-electronic charge within this part of the molecule. The average C−C bond distance in the piperidine ring is 1.56 Å and is in good agreement with the corresponding value in the crystal structure of Ni $(NCS)_2I(Pip)$ [7]. The bond angles are also close to those for a tetrahedral surrounding of each atom, caused by a chair conformation of the ring with an sp^3-hybridization.

Crystal packing shown in the projection along axis *b* (Fig. 1) is mainly determined by the van der Waals interactions. No intermolecular distances shorter than the sum of van der Waals radii were observed.

IR Spectra

Positions of relevant bands in the spectra of the ligand and the complex are in good agreement with the findings of x-ray analysis. Thus, the spectrum of non-

Table 2. Bond distances (Å) and bond angles (°) in Cu(*L*)*Pip*

Cu−O(1)	1.908 (5)	N(1)−C(1)	1.310 (9)	C(7)−C(8)	1.381 (11)
Cu−N(3)	1.942 (6)	N(2)−N(3)	1.403 (7)	C(8)−C(9)	1.422 (10)
Cu−N(4)	2.037 (6)	N(3)−C(3)	1.294 (9)	N(4)−C(10)	1.414 (32)
S−C(1)	1.754 (7)	C(3)−C(4)	1.449 (9)	N(4)−C(14)	1.479 (26)
S−C(2)	1.779 (12)	C(4)−C(5)	1.405 (9)	C(10)−C(11)	1.495 (28)
O(1)−C(9)	1.300 (8)	C(4)−C(9)	1.412 (9)	C(11)−C(12)	1.546 (31)
O(2)−N(5)	1.232 (8)	C(5)−C(6)	1.379 (10)	C(12)−C(13)	1.480 (29)
O(3)−N(5)	1.230 (9)	C(6)−N(5)	1.457 (8)	C(13)−C(14)	1.633 (21)

N(1)−Cu−O(1)	173.0 (5)	C(9)−C(4)−C(5)	115.8 (6)
N(3)−Cu−N(4)	174.6 (10)	C(4)−C(5)−C(6)	119.5 (7)
N(1)−Cu−N(3)	80.7 (2)	C(5)−C(6)−C(7)	121.9 (6)
N(1)−Cu−N(4)	97.3 (3)	C(5)−C(6)−N(5)	118.7 (7)
O(1)−Cu−N(3)	92.8 (2)	C(7)−C(6)−N(5)	119.4 (7)
O(1)−Cu−N(4)	89.0 (2)	C(6)−N(5)−O(2)	118.2 (6)
Cu−N(1)−C(1)	111.9 (5)	C(6)−N(5)−O(3)	119.0 (7)
N(1)−C(1)−N(2)	124.0 (6)	O(2)−N(5)−O(3)	121.6 (7)
N(1)−C(1)−S	119.4 (5)	C(6)−C(7)−C(8)	118.8 (7)
N(2)−C(1)−S	116.6 (5)	C(7)−C(8)−C(9)	122.6 (7)
C(1)−S−C(2)	102.9 (5)	C(8)−C(9)−O(1)	117.5 (6)
C(1)−N(2)−N(3)	107.6 (5)	C(8)−C(9)−C(4)	117.3 (6)
N(2)−N(3)−C(3)	115.4 (4)	C(4)−C(9)−O(1)	124.8 (7)
Cu−N(3)−N(2)	115.9 (6)	Cu−O(1)−C(9)	127.2 (4)
Cu−N(3)−C(3)	127.5 (6)	C(10)−N(4)−C(14)	112.4 (7)
Cu−N(4)−C(10)	112.0 (15)	C(11)−C(10)−N(4)	122.5 (19)
Cu−N(4)−C(14)	112.4 (11)	C(10)−C(11)−C(12)	112.5 (15)
N(3)−C(3)−C(4)	122.8 (7)	C(11)−C(12)−C(13)	111.3 (8)
C(3)−C(4)−C(5)	116.7 (6)	C(12)−C(13)−C(14)	104.2 (12)
C(3)−C(4)−C(9)	123.5 (6)	C(13)−C(14)−N(4)	104.8 (13)

coordinated ligand contains in the region of 3 500–3 000 cm^{-1} three characteristic bands, viz. at 3 430, 3 300 and a broader one at 3 180–3 080 cm^{-1}, corresponding to the $\nu_{as}(NH_2)$, $\nu_s(NH_2)$ and $\nu(OH)$, respectively. On the other hand, in the spectrum of the complex in the same region there are only two narrow bands at 3 370 and 3 280 cm^{-1} which can be ascribed to the $\nu(NH)$ of the deprotonated NH_2 group of H_2L and the coordinated piperidine, respectively. The $\nu(OH)$ is missing in the spectrum of the complex.

Finally, the $\nu(CN)$ band of the azomethine group, observed in the ligand spectrum at 1 620 cm^{-1} in the spectrum of the complex, is located at 1 560 cm^{-1}. The shifts of the $\nu(NH)$ and $\nu(CN)$ bands and the disappearance of the $\nu(OH)$ band are the consequence of coordination of the oxygen and nitrogen atom of the corresponding groups, i.e., of the ligand bonding in its dianionic form.

Magnetic Moment

As already mentioned, μ_{eff} of the synthesized complex is higher than for other copper complexes with (un)substituted salicylaldehyde S-methylisothiosemicarba-

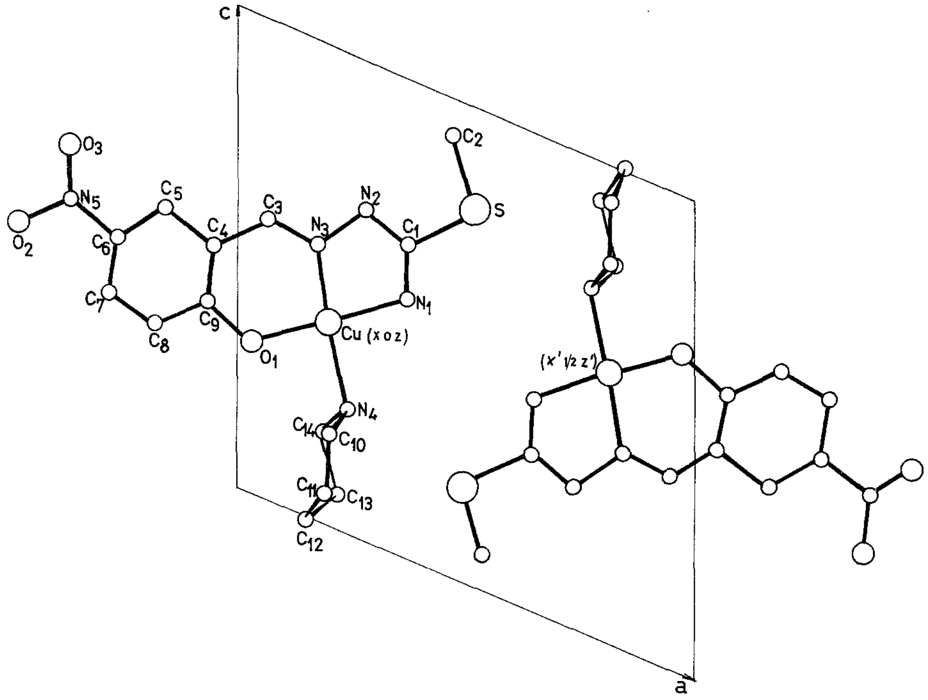

Fig. 1. The packing of molecules in the unit cell along *b*; the H atoms are omitted for clarity

zones. Due to the absence of either direct or indirect contact of the copper atoms of two neighbouring molecules, any interaction of the electron spins of two neighbouring metal centres is hindered, and, as a result, they are stabilized in the singlet state. There is no doubt that a certain contribution to forming the magnetically isolated molecules of the complex (i.e., of its monomers) has the presence of the strong electron-accepting NO_2 group in the benzene ring. As the result of its inductive effect, the electrons of the potential bridging atoms are withdrawn and thus the bridge formation ability diminished. It should be mentioned that the related complex Cu(*L*)*Im*H having a dimeric tetragonal pyramid structure with the NH bridging group is characterized by $\mu_{\text{eff}} = 1.80$ B.M. [6].

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