DALTON

Copper(II) and cobalt(II) complexes of methyl 2-pyridyl ketone thiosemicarbazone (HL); single-crystal structure of [Cu(HL)L]NCS

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The complexes $[M(HL)L]ClO_4$ (HL = methyl 2-pyridyl ketone thiosemicarbazone; M = Cu **1** or Co **2**) have been prepared from the reaction of HL with the appropriate perchlorate salt; [Cu(HL)L]NCS **3** was also prepared by transmetallation of $[Pb_2(HL)L(NCS)_2]NCS$ with an excess of copper(II) perchlorate. The new complexes have been characterized by spectroscopic techniques and the crystal structure of **3** has been determined: green triclinic crystal, $a = 10.150(2)$, $b = 10.350(2)$, $c = 11.890(2)$ Å, $\alpha = 88.55(3)$, $\beta = 83.28(3)$, $\gamma = 63.26(3)$°, space group $P\bar{1}$, $Z = 2$. The copper atom is six-co-ordinated by two NNS donor sets from terdentate ligands.

Thiosemicarbazide derivatives have raised considerable interest in chemistry and biology due to their pharmacological properties. In some cases the highest activity is associated with a metal complex, in particular copper(II) complexes are found to be more active than the corresponding uncomplexed thiosemicarbazone and are among the most potent antiviral, antitumour and antiinflammatory agents.[1–4] The mechanism by which such copper complexes and others containing thiosemicarbazone exert their biological activity is not clear. The relationship between structural and biological properties of copper(II) thiosemicarbazone complexes of different stoichiometries has been reviewed.[5]

Although considerable effort has been directed towards the isolation and characterization of new complexes, few crystal structures of metal-ion thiosemicarbazone complexes have been determined. Most crystal studies have been reported for four-co-ordinate nickel(II) and copper(II) thiosemicarbazone complexes where the ligand is co-ordinated *via* the thione or thiol sulfur and the hydrazinic nitrogen atoms.

As part of a programme concerning the behaviour of thiosemicarbazones we have recently studied complexes of Cu^{II} and Pb^{II} derived from 3,5-diacetyl-1,2,4-triazole thiosemicarbazone[6] and those of Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} and Hg^{II} derived from benzil (1,2-diphenylethanedione) thiosemicarbazone.[7,8] To extend the knowledge in this research field particularly with respect to the co-ordination properties of the heterocyclic thiosemicarbazones and the stereochemistry and molecular structures of the complexes, we now report on the synthesis and characterization of new copper(II) and cobalt(II) complexes with methyl 2-pyridyl ketone thiosemicarbazone (HL), $[M(HL)L]ClO_4$ (M = Cu **1** or Co **2**) and [Cu(HL)L]NCS **3**, together with the single-crystal structure of **3**. The isolation and characterization of the latter is important since it reveals the behaviour of the ligand as a planar NNS donor set which generates a tricyclic ligating system with the copper(II) ion in a six-co-ordinate environment.

Experimental

Measurements

Elemental analyses (C, H and N) were carried out on Perkin-Elmer model 2400 automatic equipment. Infrared spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Bomen-Michelson spectrophotometer, electronic spectra, in dimethylformamide (dmf) solution, on an Ati-Unicam UV2 spectrophotometer. Conductivity data were measured using freshly prepared dmf solutions (*ca.* 10^{-3} mol dm^{-3}) at 25 °C with a Metrohm Herisau model E-518 instrument. Mass spectra were recorded on a VG Auto Spec spectrometer.

Materials

Thiosemicarbazide, copper(II) perchlorate hexahydrate and cobalt(II) perchlorate hexahydrate were commercially available (Aldrich-Chemie) and used without further purification. Lead(II) thiocyanate were prepared according to standard procedures. **CAUTION**: perchlorate salts are potentially explosive and should be handled with care.

Preparations

Methyl 2-pyridyl ketone thiosemicarbazone (HL) was prepared using published procedures.[9,10]

$[Cu(HL)L]ClO_4$ 1. To a methanolic solution (25 cm^3) of HL (0.39 g, 2 mmol) was added dropwise with stirring a methanolic solution (25 cm^3) of $Cu(ClO_4)_2·6H_2O$ (0.38 g, 1 mmol) at room temperature. After 2 h of continuous stirring the solution changed to green. A green solid was isolated after slow evaporation of the solvent, washed with MeOH and Et_2O and dried *in vacuo*: yield = 50% (Found: C, 34.55; H, 3.75; N, 20.45. $C_{16}H_{19}ClCuN_8O_4S_2$ requires C, 34.5; H, 3.45; N, 20.4%).

$[Co(HL)L]ClO_4$ 2. To a methanolic solution (25 cm^3) of HL (0.39 g, 2 mmol) was added dropwise with stirring a methanolic solution (25 cm^3) of $Co(ClO_4)_2·6H_2O$ (0.37 g, 1 mmol) at room temperature. After 2 h of continuous stirring the solution changed to brown. A brown solid was isolated after slow evaporation of the solvent, washed with MeOH and Et_2O and dried *in vacuo*: yield = 87% (Found: C, 34.75; H, 2.80; N, 20.25. $C_{16}H_{19}ClCoN_8O_4S_2$ requires C, 35.2; H, 3.50; N, 20.55%).

[Cu(HL)L]NCS 3. Compound **3** was isolated by changing the experimental conditions. Since previous studies[6,11,12] had indicated a high degree of lability of Pb^{II}, in order to synthesize new copper complexes we tried transmetallation reactions as follows: to a hot (60 °C) methanolic suspension (25 cm^3) of lead(II) thiocyanate (0.32 g, 1 mmol) was added dropwise with stirring a methanolic solution (25 cm^3) of HL (0.19 g, 1 mmol). After 2 h of continuous stirring a yellow solid was isolated for which the elemental analysis and mass spectrum corresponded to the complex $[Pb_2(HL)L(NCS)_2]NCS$: yield = 75% (Found: C, 23.3; H, 1.80; N, 15.95%; *m/z* 977 calc.: C, 23.35; H, 1.95; N, 15.8%). The required complex **3** was obtained by stirring a methanolic suspension of $[Pb_2(HL)L(NCS)_2]NCS$ (0.99 g, 1 mmol) with a methanolic solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (2.28 g, 6 mmol) at room temperature. After 2 h of continuous stirring a green solution was obtained. After slow evaporation of the solvent to half volume, the solution was kept in a cool place. In a few weeks good green crystals suitable for X-ray analysis were obtained: yield = 52% (Found: C, 40.25; H, 3.05; N, 24.25. $C_{17}H_{19}CuN_9S_3$ requires C, 40.1; H, 3.75; N, 24.8%).

Attempts to prepare [Co(HL)L]NCS by transmetallation reaction from $[Pb_2(HL)L(NCS)_2]NCS$ and $Co(ClO_4)_2{\cdot}6H_2O$ were unsuccessful, the product being identified as the previously mentioned compound **2**.

Crystallography

A summary of the data collection and details of the structure refinement is given in Table 1. A green prismatic crystal was mounted on a Siemens R3m/V difractometer at 293 K. The cell dimensions were refined by least-squares methods to the Bragg angles of 25 reflections. The intensities were corrected for Lorentz-polarization effects. The structure was solved by Patterson and Fourier methods using SHELXTL PLUS program[13] and an empirical absorption correction was applied.[14] The final full-matrix least-squares refinement was made with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the thiocyanate atoms. Hydrogen atoms could not be located; the function minimized was $\Sigma w(\Delta F)^2$ with $w^{-1} = \sigma^2(F_o)$. Atomic scattering factors were those included in SHELXTL PLUS.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/115.

Results and Discussion

Crystal and molecular structure

A drawing of the complex with the atomic numbering scheme is shown in Fig. 1 and selected bond lengths and angles in Table 2. The structure consist of discrete $[Cu(HL)L]^+$ cations and SCN^- anions, the two ligands show *E* configuration[15] about N(10)–C(11); the organic molecule acts as a terdentate ligand with the NNS donor set placed on the same side. The coordination sphere of the copper can be described as a distorted octahedron with imine nitrogen atoms in the axial positions and the four equatorial positions occupied by two sulfur and two pyridine nitrogen atoms. The ligands are not equivalent because one has lost the N^2 proton (L) whereas the other is neutral (HL); the right and left halves of the figure are slightly different. The two ligands are in the *mer* configuration (azomethine nitrogen atoms *trans*) as found in other octahedral thiosemicarbazone complexes[16–18] and the angle between them is 90.1°. Each of the ligands consist of three rings, one heterocyclic and two chelates. The presence of the tricyclic ring system gives a planar structure around the metal which contributes to the stability of the copper(II) state.[19]

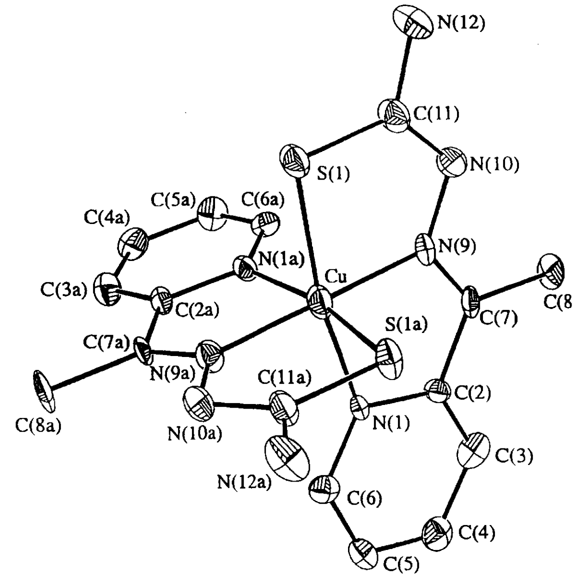

Fig. 1 Crystal structure of the complex [Cu(HL)L]NCS **3**

Examination of the bond length data shows that the C–N distances N(10)–C(11) 1.361 and N(10a)–C(11a) 1.379, N(12)–C(11) 1.379 and N(12a)–C(11a) 1.364 Å in the side chain of the ligands are intermediate between formal single and double bonds and are comparable with those reported for other thiosemicarbazone metal complexes.[20,21] However, the C–S distances [C(11)–S(1) 1.762 and C(11a)–S(1a) 1.773 Å] are some of the largest found for thiosemicarbazone complexes, typical bond lengths being C(sp^2)–S 1.760 Å in $(MeS)_2C{=}C(SMe)_2$, and

Table 1 Experimental data for the crystallographic analysis of complex **3**

Formula	$C_{17}H_{19}CuN_9S_3$
M	509.13
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.150(2)
b/Å	10.350(2)
c/Å	11.890(2)
α/°	88.55(3)
β/°	83.28(3)
γ/°	63.26(3)
$U/Å^3$	1107.3(4)
λ(Mo-Kα)/Å	0.710 73
Z	2
$D_c/g\ cm^{-3}$	1.530
F(000)	524
Crystal size/mm	0.1 × 0.5 × 0.08
μ/mm^{-1}	1.291
2θ Range/°	3.0–45
hkl Ranges	−1 to 8, −10 to 11, −12 to 12
Independent reflections	3214
Observed reflections	2134
Maximum, minimum height in final Δ*F* map/e $Å^{-3}$	1.03, −0.94
No. parameters refined	256
Final *R*, *R'*	0.07, 0.10

Table 2 Selected bond lengths (Å) and angles (°)

Cu–S(1)	2.257(3)	N(9)–C(7)	1.365(11)
Cu–S(1a)	2.273(5)	N(10)–C(11)	1.361(12)
Cu–N(1)	1.997(7)	N(12)–C(11)	1.379(13)
Cu–N(9)	1.936(7)	N(1a)–C(2a)	1.416(13)
Cu–N(1a)	1.997(12)	N(1a)–C(6a)	1.389(16)
Cu–N(9a)	1.940(9)	N(9a)–N(10a)	1.405(16)
S(1)–C(11)	1.762(10)	N(9a)–C(7a)	1.330(18)
S(1a)–C(11a)	1.773(11)	N(10a)–C(11a)	1.379(19)
N(1)–C(2)	1.430(11)	N(12a)–C(11a)	1.364(20)
N(1)–C(6)	1.359(13)	S(1b)–C(1b)	1.783(27)
N(9)–N(10)	1.382(11)	N(1b)–C(1b)	1.282(29)
S(1)–Cu–S(1a)	90.9(1)	N(1)–Cu–N(1a)	90.4(4)
S(1)–Cu–N(1)	169.2(2)	N(9)–Cu–N(1a)	97.1(4)
S(1a)–Cu–N(1)	90.3(3)	S(1)–Cu–N(9a)	94.2(2)
S(1)–Cu–N(9)	85.9(2)	S(1a)–Cu–N(9a)	85.8(4)
S(1a)–Cu–N(9)	94.2(4)	N(1)–Cu–N(9a)	96.7(3)
N(1)–Cu–N(9)	83.3(3)	N(9)–Cu–N(9a)	180.0(7)
S(1)–Cu–N(1a)	90.5(2)	N(1a)–Cu–N(9a)	82.8(4)
S(1a)–Cu–N(1a)	168.6(2)	S(1b)–C(1b)–N(1b)	174.7(17)

Table 3 Selected vibrational bands (cm^{-1}) of HL and its complexes

	HL	**1**	**2**	**3**
$\nu_{asym}(NH_2)$	3362	3341	3289	3407
$\nu_{sym}(NH_2)$	3256	3290	3265	3293
ν(NH)	3186	3158	3136	3164
ν(SCN)	—	—	—	2052
$\delta(NH_2)$ + ν(CN)	1607	1650, 1627	1616, 1599	1628
py ν(CN) + ν(CC)	1582	1587	1578	1598
Thioamide I	1500	1507	1496	1495
Thioamide II	1426	1473	1442	1450
Thioamide III	1149	1165	1179	1177
$\nu_3(ClO_4)$		1088	1108	—
py breathing	994	1032	1086	1021
Thioamide IV	850	790	816	825
$\nu_4(ClO_4)$		625	626	—
py 16a	624	632	628	648
py 16b	404	409	408	412

C=S 1.630 Å in naphthylphenyl thioketone.[22–25] This substantiates a certain displacement of the tautomeric equilibrium to the thiol form and also confirms the importance of the resonance structures for HL and L and shows how the electronic flexibility of the thiosemicarbazone system allows it to lose or keep a positive charge without significantly altering its ligating properties.

The equatorial sites in the complex are occupied by the pyridine nitrogen and the sulfur atoms with bond lengths and angles N(1)–Cu 1.997 and N(1a)–Cu 1.997, S(1)–Cu 2.257 and S(1a)–Cu 2.273 Å, N(1)–Cu–N(1a) 90.4 and S(1)–Cu–S(1a) 90.9° and two imino nitrogen atoms in the axial sites, N(9)–Cu–N(9a) 180°. The bond lengths N(9)–Cu 1.936 and N(9a)–Cu 1.940 Å are shorter than the equatorial distances as expected for tetragonally distorted octahedral '2 + 4' co-ordination (two short and four long bonds). The reason for this is ascribed to the Jahn–Teller effect when a d^9 ion is subjected to an octahedral crystal field. The thiocyanate ion, C(1b)–N(1b) 1.282, C(1b)–S(1b) 1.783 Å and N(1b)–C(1b)–S(1b) 174.7° is not co-ordinated but is involved in a hydrogen-bonding network.

The three dimensional packing is formed by double intermolecular bonds between cations and thiocyanate anions: N(12)–H $\cdots$ S(1b) ($x - 1$, $y + 1$, z) 3.397 Å and 156.4° and N(12)–H $\cdots$ N(1b) ($-x$, $-y$, $1 - z$) 2.970 Å and 146.9°; these bonds link the molecules into polymeric ribbons along the *c* axis.

Infrared spectra

The main vibrational bands of free HL and its complexes are compared in Table 3. That of the bands in the 3500–3100 cm^{-1} region is made difficult owing to the presence in the complexes of both the un- and mono-deprotonated forms and of numerous hydrogen-bonding interactions (NH $\cdots$ N and NH $\cdots$ S). The displacements to higher wavenumbers of the bands arising from the pyridine upon complexation and the positive shift of the azomethine nitrogen illustrate participation of the pyridine and imine nitrogen atoms in the co-ordination. Also all the complexes show significant changes in the 1550–700 cm^{-1} region (thioamide I–IV bands),[26] the negative shift in the thioamide IV band is consistent with co-ordination through the sulfur of the thioamide group. Therefore, these data indicate that the ligand is tridentate in these complexes.

The spectra of the perchlorate complexes show ν_3 (1100 cm^{-1}) and ν_4 (625 cm^{-1}) fundamental vibrational modes of the anion (T_d symmetry) and the spectrum of the thiocyanate complex shows a band at 2052 cm^{-1} ($C_{\infty v}$ symmetry). Together with the conductivity data in the range 60–90 Ω^{-1} cm^2 mol^{-1} in dmf for all the complexes according to a 1 : 1 electrolyte behaviour, these data confirm the ionic form of the counter ions.

UV/VIS spectra

The electronic absorption spectra of the complexes are dominated by an intense band centred at *ca.* 390, 425 and 410 nm for **1**, **2** and **3** assigned to S→M and N(py)→M ligand-to-metal charge transfer transitions. This band may also include an intraligand component (380 nm for uncomplexed HL). The d–d bands are observed at *ca.* 605 and 595 nm for **1** and **3** respectively and 590 nm for **2**. All point to a distorted-octahedral environment for the metal ions as found for previously.[27–29]

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