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Preparation, crystal structure and reactivity of bis(2-thioxohexamethyleneimine)copper(I) iodide

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Abstract

The complex bis(2-thioxohexamethyleneimine)copper(I) iodide, hereafter mentioned as Cu(tclH)$_2$I, has been synthesized and studied by means of spectroscopic methods and single crystal X-ray diffraction. It crystallizes in the $P2_1/n$ space group, with $a = 28.193(4)$, $b = 8.611(1)$, $c = 6.896(1)$ Å, $\beta = 90.81°$ and $Z = 4$. The chromophore is planar, the mean value of the two Cu–S bonds being 2.441(1) Å and the Cu–I bond 2.590(1) Å. The interbond angles around copper lie close to 120°. The reactivity of the complex towards small molecules (e.g. CS$_2$, CO) and Lewis bases (e.g. pyridine, PPh$_3$, AsPh$_3$), is also discussed.

Introduction

The study of Cu(I) complexes with ligands possessing N and S donor atoms is essential in the effort to gain insight into the bonding and stereochemistry of the copper ions, which participate in a number of potential enzymic sites [1]. As a contribution to this field of research we have long been engaged in the study of the coordination of heterocyclic thiones towards copper(I) [2], placing particular emphasis on the determination of the stereochemistry of the metal center and the coordination mode adopted by the ligands, which is affected by the thiol–thione equilibrium [3]. When this equilibrium is notably shifted towards one of the tautomers, thiones provide excellent media for the study of 'pure' metal–ligand bond nature and reactivity. In this study, we considered 2-thioxohexamethyleneimine (ω-thiocaprolactam) [4, 5], since it combines the potential NH–C=S binding site and has been successfully tested as analytical reagent [6], as fungicidal [7] and as absorption promoter [8] for other active pharmaceutical agents. Furthermore, the spectral studies of its complexes towards Cu, Rh and Pt reported [4] suggest binding through sulfur, but the only structural study reported is that of a Rh dimer compound [4a], where the deprotonated form of the ligand is present with both S and N atoms participating in the bonding.

In the present study, we report on the synthesis, crystal structure determination and reactivity of the complex Cu(tclH)$_2$I.

Experimental

Materials and measurements

All the solvents used were of reagent grade. Copper iodide and CO (Merck) were used as obtained, while ω-thiocaprolactam (Aldrich) was recrystallized from hot methanol prior to its use.

The elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 elemental analyzer. The IR spectra were recorded in KBr discs on a Perkin-Elmer 467 spectrophotometer, while the electronic spectra were obtained by means of a Perkin-Elmer-Hitachi 200 spectrophotometer. A Bruker AW-80 spectrometer was used for the recording of the ^{1}H NMR spectra. The chemical shifts obtained in deuteriated chloroform solutions are reported in (δ, ppm) downfield from internal TMS standard.

Preparative

A solution of 3 mmol of tclH in 10 ml methanol was added to 1 mmol CuI suspended in 20 ml hot methanol. The resulting yellow solution was heated

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for 15 min, after which, it was filtered and the filtrate allowed to stay at room temperature for two days. During this period, pale yellow crystals of the title compound were deposited and were filtered and dried in vacuum. *Anal.* Calc. $Cu(tclH)_2I$: C, 32.10; H, 5.34; N, 6.24. Found: C, 31.5; H, 5.53; N, 6.41%. The collected crystals were appropriate for X-ray diffraction study.

Solution of the structure

Complete crystal data and parameters for data collection are reported in Table 1. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 15 automatically centered reflections in the range $50° < 2\theta < 54°$ on a Syntex $P2_1$ diffractometer with Ni-filtered Cu $K\alpha$ radiation. The intensities of three standards monitored after 67 reflections were stable with a scatter of less than 3% from their respective means. Lp and absorption corrections were applied. The atomic scattering factors were taken from the International Tables for

TABLE 1. Summary of crystal and intensity collection data

Formula	$CuIS_2N_2C_{12}H_{22}$
Formula weight	448.9
a (Å)	28.193(4)
b (Å)	8.611(1)
c (Å)	6.896(1)
β (°)	90.81(1)
V (Å^3)	1674.1(5)
Z	4
D_{calc} (Mg m^{-3})	1.780
D_{meas} (Mg m^{-3})	1.810
Space group	$P2_1/n$
Crystal dimensions (mm)	$0.11 \times 0.11 \times 0.25$
Radiation	Cu $K\alpha$
μ (cm^{-1})	185.94
Transmission factors	0.0771–0.2910
Scan speed (°/min)	2.5–18.0
Scan range (°)	1.6 plus α_1–α_2
Background counting (s)	0.8 of scan time
2θ limit (°)	125.0
Data collected	3115
Data unique	2666
R_{int}	0.0171
Data used	2513 with $F_o > 4.5\sigma(F_o)$
Range of hkl	$-32 \rightarrow 32$, $0 \rightarrow 9$, $-7 \rightarrow 0$
Weighting scheme	$1/w = s2(F_o) + 0.0001F_o^2$
$F(000)$	904
No. refined parameters	252
$\lvert\Delta/\sigma\rvert_{max}$	0.154
$(\Delta\rho)_{max}$ (eÅ^{-3})	0.435
$(\Delta\rho)_{min}$ (eÅ^{-3})	−0.512
R^a (obs.)	0.0207
R (all data)	0.0226
$R_w{}^b$ (obs.)	0.0259
$R_w{}^b$ (all data)	0.0263

[a] $R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$. [b] $R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$.

TABLE 2. Position and equivalent thermal parameters ($\times 10^4$) of the non-hydrogen atoms[a]

Atom	x	y	z	U
I	1257.6(1)	3368.7(2)	11187.1(3)	482
Cu	1173.9(1)	2377.6(5)	7653.5(7)	465
S(1)	1790.8(2)	1278.2(9)	6141(1)	462
S(2)	486(3)	2567(1)	6012(1)	617
C(11)	2232(9)	819(3)	7737(4)	378
N(12)	2186.3(9)	960(3)	9602(4)	485
C(13)	2550(1)	653(5)	11096(5)	609
C(14)	2973(1)	1736(5)	10992(6)	654
C(15)	3310(1)	1369(5)	9391(6)	623
C(16)	3099(1)	1428(4)	7359(6)	534
C(17)	2698(1)	275(4)	6970(5)	445
C(21)	24.4(9)	2715(4)	7540(4)	450
N(22)	77.2(9)	2848(3)	9393(4)	476
C(23)	−298(1)	3001(4)	10841(5)	536
C(24)	−602(1)	1557(5)	10998(6)	615
C(25)	−953(1)	1351(5)	9353(7)	635
C(26)	−735(1)	1187(5)	7379(6)	627
C(27)	−471(1)	2639(5)	6713(5)	553

[a] e.s.d.s in parentheses. $U_{eq} = U_{11} + U_{22} + U_{33})/3$.

TABLE 3. Interatomic distances (Å) and angles (°) for $Cu(tclH)_2I$

Bond lengths			
Cu–I	2.590(1)	C16–C15	1.515(9)
S1–Cu	2.250(1)	C17–C16	1.527(7)
S2–Cu	2.238(1)	N22–C21	1.290(7)
C11–S1	1.696(5)	C27–C21	1.502(7)
C21–S2	1.691(5)	C23–N22	1.472(6)
N12–C11	1.300(6)	C24–C23	1.514(8)
C17–C11	1.498(6)	C25–C21	1.506(10)
C13–N12	1.467(7)	C26–C25	1.509(10)
C14–C13	1.518(10)	C27–C26	1.529(10)
C15–C11	1.501(10)		
Bond angles			
S1–Cu–I	120.9(0)	C17–C16–C15	114.9(5)
S2–Cu–I	121.3(0)	C16–C17–C11	112.7(4)
S2–Cu–S1	117.8(1)	N22–C21–S2	123.0(4)
C11–S1–Cu	111.2(2)	C27–C21–S2	118.6(4)
C21–S2–Cu	111.0(2)	C27–C21–N22	118.3(5)
N12–C11–S1	122.6(4)	C23–N22–C21	127.3(4)
C17–C11–S1	118.8(4)	C24–C23–N22	112.8(5)
C17–C11–N12	118.6(4)	C25–C24–C23	114.2(5)
C13–N12–C11	126.9(5)	C26–C25–C24	114.7(5)
C14–C13–N12	113.4(5)	C27–C26–C25	113.7(5)
C15–C14–C13	114.3(5)	C26–C27–C21	112.0(5)
C16–C15–C14	115.4(5)		

Hydrogen bonds

A	B	C	A–B	B–C	A–C	A–B–C
N12	–H21	···I	0.80(4)	2.75(3)	3.526(3)	165(3)
N22	–H22	···I	0.83(3)	2.75(3)	3.562(3)	170(3)

X-ray Crystallography [9]. The crystal structure was solved by direct methods and the positional and thermal parameters were refined with SHELX76 [10] by full-matrix least-squares in which $\Sigma w\Delta^2$ was minimized. Hydrogen atoms were located by a difference of Fourier map. One reflection showing poor agreement was given zero weight during the final refinement cycles. The final atomic parameters of the non-H atoms are given in Table 2, bond lengths and angles in Table 3.

Results and discussion

Description of the structure

The complex is a three-coordinate monomer with the molecules well separated from each other. The monomer structure is presented in Fig. 1 and selected bond lengths and angles in Table 3. The Figure, in accordance with the elemental analysis, reveals a copper coordination sphere consisting of two tclH ligands and an iodine atom.

The two Cu–S bonds are nearly equal, their mean value (2.244(1) Å) being close to that observed [11] in the case of $[Cu(SPMe_3)_3]^+$ (2.259(5) Å), tris(tetramethylthiourea)copper(I)tetrafluroborate (2.25(1) Å) and of tris(ethylenethiourea)copper(I) cation (2.27(1) Å), and appreciably shorter than the simple Cu–S bond, indicating that the ligand retains much of its thione character in the complexes. On the contrary, they are relatively longer than the bond lengths reported [12, 2] for typical trigonal three-coordinate copper(I) complexes with sulfur ligands. The relative elongation of the Cu–S bonds may be attributed to the bulky thione ligand, which 'crowds' the coordination environment of copper, which is elevated by 0.004 Å from the plane defined by the donor atoms S(1), S(2) and I.

The Cu–I distance (2.590(1) Å) is also longer than that observed in planar trigonal Cu(I) iodide complexes [13], a fact that may be attributed to the intramolecular I···H interaction which is detected. The observed I···H distance of 2.75(3) Å, meets Hamilton's criterion [14] for hydrogen bond formation, being 0.65 Å shorter than the sum of the van der Waals radii of I and H. The hydrogen atom participating in this hydrogen bond is the NH hydrogen; its approach to I is facilitated by a symmetrical twist of the two tclH ligands with respect to the Cu–I axis.

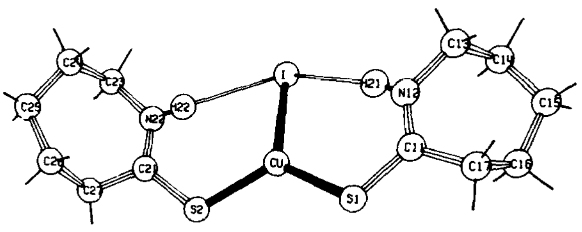

Fig. 1. A view of the $Cu(tclH)_2I$ molecule.

The C–S bonds retain partially their double bond character, their bond lengths being 1.696(5) Å and 1.691(5) Å, respectively, while substantial double bond character is detected for the adjacent C–N bonds, for which bond lengths of 1.300(6) and 1.290(7) Å are observed.

The interbond angles around copper are close to 120°, while the Cu–S–C angles are in the range of the previously reported ones for coordinated thione molecules [15, 12e], while the copper environment is essentially planar, the dihedral angle between the planes defined by Cu,I,S(1) and Cu,I,S(2), respectively being only 0.5°.

Spectral and reactivity study

The IR spectrum of the title compound consists of absorption bands analogous to those already reported [5] for the corresponding chloride and bromide compounds. The characteristic NH stretching vibration, observed at 3190 cm^{-1} in the free ligand remains practically unshifted, indicating the monodentate through sulfur coordination. The UV–Vis spectrum in methanol is dominated by a strong band at 277 nm, accompanied by a shoulder at 308 nm. The latter, must be attributed to a MLCT excitation, since no analogous absorption is present in the spectrum of the free ligand. The ^1H NMR is also similar to those recorded for the aforementioned compounds [5]; the imine hydrogen is found to resonate at 10.38 ppm and the rest protons are detected in the regions 3.45 (m, 2H), 2.82 (m, 2H) and 1.70 m (m, 6H) ppm, respectively.

Upon treatment with equimolar amounts of NaOH or $NaHCO_3$ in methanol, the compound reacted forming an orange solid product. Its formula was identified as $[Cu(tcl)]_x$ on the basis of its elemental analysis, its IR spectral data (absence of the –NH band and broadening of the rest of the bands, especially those due to C=S and C–N) as well as its comparison against an originally prepared sample, formed by the reaction of CuI with deprotonated tcl^- at a 1:1 molar ratio.

Chloroform and methanol solutions of $Cu(tclH)_2I$ appear to be fairly stable in air and not significantly affected by moisture. In view of the three-coordinate Cu(I) environment, it seemed reasonable to investigate the reactivity [16] towards small molecules and the possibility of adduct formation with Lewis bases. The results of this study are summarized as follows.

(i) Carbon disulfide. The title complex is readily soluble in CS_2. After stirring for 15 min at room

temperature the solution was evaporated under reduced pressure to a third of its original volume, which was then allowed to further evaporate at room temperature. The obtained product revealed a medium strength IR absorption at 645 cm^{-1} attributed to coordinated CS_2. Its UV–Vis spectrum in methanol, revealed an extended plateau (330–365 nm), accompanied by a distinct shoulder at 376 nm. The ^1H NMR spectrum reveals a slight downfield shift of the tclH protons with respect to the original compound (NH proton at 9.88 ppm, carbon protons at 3.50 (m,2H), 2.88 (m,2H) and 1.84 (m,6H) ppm, respectively).

(ii) Pyridine. Observations analogous to the aforementioned ones were made in the case of reaction with pyridine. Owing to the low affinity of pyridine towards Cu(I) centers [17] pyridine was used as the solvent. The complex dissolved readily and the UV–Vis spectrum of the product showed a red shift (distinct shoulder (342 nm) of a main band appearing at 325 nm), with respect to the spectrum of $Cu(tclH)_2I$, which is indicative of pyridine adduct formation [17]. The NMR spectrum is similar though not identical to the one recorded in the previously discussed case (NH proton at 10.25 ppm, carbon protons at 3.47 (m,2H), 2.93 (m,2H) and 1.77 (m,6H) ppm, respectively) with the addition of the pyridine protons in the region 7.40–8.40 ppm. The adduct is by no means stable, since moderate heating or a two-day stay at room temperature causes the elimination of the pyridine molecules, as evinced by the diminishing of the corresponding proton signals in the NMR and the discussed shoulder in the UV–Vis spectrum, respectively.

(iii) Carbon monoxide. A chloroform solution of the title complex was treated with CO under a pressure of 2 atm. for 10 min. Only a slight darkening of the colour was observed. The solution IR spectrum of the product revealed a strong absorption at 1730 cm^{-1}, indicative of CO insertion in the complex, presumably in a bridging fashion. The band appears considerably lower than the corresponding one in other Cu(I)–CO systems [18], but this may be explained in terms of the stronger electron withdrawing ability of tclH relative to the amine molecules which are coordinated to the Cu(I) center in the aforementioned cases. Therefore, in the electron poor environment of Cu(I) in our case, the Cu–C overlap becomes stronger, eventually leading to elongation of the C=O bond.

(iv) Group V donor atoms. Reactions with 1:1 molar ratio of PPh_3 and $AsPh_3$ in mixed $MeOH:CHCl_3$ and MeOH:toluene solutions, with moderate heating, afforded the mixed ligand complexes $Cu(tclH)(PPh_3)_2I$ and $Cu(tclH)_2(AsPh_3)I$, respectively. The compounds were identified by elemental analyses and their spectral data. The lower yield (*c.* 40% relative to 75%) of the reaction with $AsPh_3$ is indicative of the lower donor ability of the As atom. Reaction with $SbPh_3$ under the same conditions produced a dark brown precipitate, owing to the well-known thermal instability of the $SbPh_3$ ligand. The reactions were also carried out in different molar ratios in order to force the formation of the corresponding $Cu(tclH)_2(PPh_3)I$ and $Cu(tclH)(AsPh_3)_2I$ compounds but the stoichiometry of the products was the same as above in every case.

(v) Pyridine-2-thione. Finally, in an effort to estimate the relative reactivity of thiones a methanolic solution of $Cu(tclH)_2I$ was treated with an equimolar amount of pyridine-2-thione. Upon refluxing the solution, an orange precipitate formed; its spectral data were identical to those of $Cu(py2SH)_2I$. The reaction proceeded at room temperature as well, affording after a prolonged stay (8 days) the same product.

Conclusions

The bulky ω-thiocaprolactam is found to readily coordinate to CuI, giving rise to a monomer three-coordinated complex. The compound is subject to facile uptake of small molecules and Lewis bases, a reactivity which has been fully confirmed by experiment. The discussed reactions are of importance since they occur in a Cu(I)–thione system, which plays a key role in several biochemical interactions, and may therefore serve as models for such interactions.

Supplementary material

Tables of fractional coordinates for hydrogen atoms, isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms are available on request from the authors.

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