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The crystal structure, equilibrium and spectroscopic studies of bis(dialkyldithiocarbamate) copper(II) complexes $[Cu_2(R_2dtc)_4]$ (dtc=dithiocarbamate)

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Abstract

Four copper(II) complexes of bis(dialkyldithiocarbamate) $[Cd(R_2dtc)_2]$ (R=Me, Et, Pr, *i*-Pr; dtc=dithiocarbamate) have been prepared and characterized by elemental analysis, IR and ESR spectra studies. Their equilibrium constants (*K*), determined by a UV-vis spectrometry in EtOH, were influenced by the alkyl groups in the following order: *i*-Pr>*n*-Pr≈Et>Me. The single crystal structures of complex $[Cu_2(R_2dtc)_4]$ have been determined using X-ray diffraction methods. The compounds $[Cu_2(Et_2dtc)_4]$ and $[Cu_2(Pr_2dtc)_4]$ are built of centrosymmetric neutral dimeric $[Cu_2(R_2dtc)_4]$ entities. The copper atom lies in a distorted square–pyramidal environment. The four equatorial donors are two bidentate chelate sulfur atoms from two dtc ligands. One of the sulfur atoms from the third dtc ligand acts as a bridging ligand occupying the apical position of the symmetry-related copper atom in the dimer structure, which is viewed as two edge-sharing distorted square–pyramids. The structure of $[Cu_2(i-Pr_2dtc)_4]$ is square planar with an exactly planar CuS₄ unit and nearly planar NCS₂ moieties. The Cu–S distances shows small decreases along the series *n*-Pr>Et>*i*-Pr, the biggest change being for the diisopropyl complex. The alkyl substituents at the nitrogen atom affect their coordination number and Cu···Cu distance. In the solid, $[Cu_2(n-Pr_2dtc)_4]$ has the shortest Cu···Cu distance and [Cu(*i* $-Pr_2dtc)_2]$ has the longest one. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal structure; Dialkyldithiocarbamate; Equilibrium constant

1. Introduction

Dialkyl-substituted dithiocarbamate anions have proved to be highly versatile chelating agents for the separation of metals as metal chelates using gas chromatography [1]. Their good performance in liquid–liquid extraction and other analytical procedures [2] makes them more attractive for the determination of metals using gas chromatography [3]. Some of dialkyl-substituted dithiocarbamate salts have also shown interesting biological effects which include anti-alkylation [4,5] or anti-HIV properties [6,7]. They are also used as effective antidotes for cadmium intoxication [8,9]. The ability of dtc to bind to metal has been known for many years. It forms a chelate with virtually all transition elements [10]. The bidentate anion is also well known as a bridge between two transition metal centers [11]. Water-soluble dialkyldithiocarbamate complexes are known to have been tested in various medical applications [12]. Dialkyldithiocarbamate sodium salts are also good extracting agents for many transition metals [13], and are good floating agents of flotation concentrate for novel metal ores and copper ores [14].

In recent years the study of binuclear copper(II) complexes has been a subject of considerable interest because of their structural, magnetic, EPR and electrochemical properties [15]. In this paper, we report infrared (IR) and EPR spectra of four copper(II) complexes of bis-(dialkyldithiocarbamate), and a study of their equilibrium

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constants. Also the crystal structure of copper(II) bis-(dialkyldithiocarbamate) complex has been determined.

2. Experimental

2.1. Physical measurements

Elemental analyses were obtained at the Analysis and Measurement Centre of Nanjing University. The IR spectra were recorded in the 4000–400 cm⁻¹ region using KBr pellets on a Nicolet 170 SX FTIR spectrometer. Magnetic measurements on powder samples were performed in the 75–300 K temperature range by means of a Faraday-type magnetometer. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer.

2.2. Synthesis

All chemicals were obtained from a commercial source and used without further purification.

2.3. Preparation of the N,N'-dialkyldithiocarbamate sodium $[Na(R_2dtc)]$

To a stirred solution of dialkyl-secondary amine (0.05 mol, Me₂NH is 40% aqueous solution) in ethanol (5 ml) was added, at less than 4°C, carbon disulfide (3.1 ml, 0.052 mol) and sodium hydroxide (50% aqueous solution, 4 ml). After stirring for 4–5 h, evaporation of the volatile was performed without heating. The pure [Na(R₂dtc)] was obtained by recrystallisation from the solution of ethanol. Yield: 80–90%.

2.4. Preparation of copper(II) complexes $[Cu(R_2dtc)_2]$

To a heated aqueous solution of Na(R₂dtc) (0.01 mol) was added an EtOH solution of Cu perchlorate [Cu(ClO₄)₂, 0.054 mol] with stirring. A brown precipitate was deposited. Upon collection by filtration, the deposit was washed with water and dried over P₄O₁₀. It was collected and submitted for elemental analysis. The analytical data on the copper(II) complexes are presented in Table 1.

2.5. X-ray structure determination

A summary of the key crystallographic information is given in Table 2. Selected bond distances and angles are listed in Table 3. The selected crystal of $[Cu_2(R_2dtc)_4]$ was mounted on a SMART CCD diffractometer. Reflection data were measured at 20°C using graphite monochromated MoK α (λ =0.71073 Å) radiation with a detector distance of 4 cm and swing angle of -35° . The collected data were reduced by using the program SAINT [16] and empirical absorption correction was carried out using the

Table 1					
Elemental	analyses	of	the	copper(II)	complexes

Complex	% C	% H	% N
$Cu(Me_2dtc)_2$	23.68	4.01	9.31
Calc.	(23.71)	(3.98)	(9.22)
$Cu(Et_2dtc)_2$	33.43	5.24	7.73
Calc.	(33.36)	(5.60)	(7.78)
$Cu(n-Pr_2dtc)_2$	40.34	7.10	7.23
Calc.	(40.41)	(6.78)	(6.73)
$Cu(i-Pr_2dtc)_2$	40.45	6.90	7.05
Calc.	(40.41)	(6.78)	(6.73)

SADABS [17] program. The structure was solved by direct methods and refined using the full-matrix least-squares method on F_{obs}^2 by using the SHELXTL [18] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were created by using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from the International Table for X-Ray Crystallography [19].

2.6. Equilibrium studies

UV-vis solution spectra were recorded on a Shimadzu UV-240 spectrophotometer at room temperature. Addition of colorless dialkyldithiocarbamate sodium EtOH solution to the EtOH solution of $[CuCl_2]$ promptly forms brown dialkyldithiocarbamate copper(II) complexes, which show the intensity characteristic absorption at a wavelength of ca. 435 nm. The stoichiometry and stability constants were determined using the method described by Job [20], and calculated using the method of Meng and Jiang [21].

3. Results and discussion

3.1. Description of the structure

The structure of complex $[Cu_2(Et_2dtc)_4]$ and $[Cu_2(n-Pr_2dtc)_4]$ is built up of centro-symmetric dimeric entities. Fig. 1 shows a perspective view of the dimeric unit with the atomic numbering scheme of $[Cu_2(n-Pr_2dtc)_4]$, and Fig. 2 a perspective view of the crystal packing in the unit cell.

The coordination sphere of the copper(II) ions is best described as a distorted square–pyramid. The basal coordination positions are occupied by four sulfur atoms belonging to two dtc ligands. The five coordination is achieved by linking to a sulfur atom from the third ligand occupying the equatorial site in the coordination polyhedron of the centrosymmetrically related copper(II) ion. Therefore, each bridging sulfur simultaneous occupies an equatorial coordination site on one copper(II) ion and an apical site on the other Cu(II). The topology of the informed dimers is then viewed as edge-sharing distorted square–pyramids. As

Table 2 Summary of crystallographic result for [Cu(R,dtc),]

Complex	$[\mathrm{Cu}_2(n-\mathrm{Pr}_2\mathrm{dtc})_4]$	$[Cu_2(Et_2dtc)_4]$	$[Cu(i-Pr_2dtc)_2]$
Empirical formula	$C_{28}H_{56}Cu_2N_4S_8$	$C_{20}H_{40}Cu_2N_4S_8$	C ₁₄ H ₂₈ CuN ₂ S ₄
Formula weight	832.32	720.12	416.17
Crystal size (mm)	$0.42 \times 0.10 \times 0.08$	$0.24 \times 0.20 \times 0.20$	$20 \times 0.30 \times 0.35$
Space group	P2(1)/c	$P2_1/c$	$P\overline{1}$
Unit cell dimensions			
a (Å)	8.3023(2)	9.9043(8)	11.582(2)
<i>b</i> (Å)	8.5756(4)	10.6127(8)	11.720(2)
c (Å)	13.2515(2)	15.496(1)	7.636(3)
α (°)	90	90	96.28(2)
β (°)	100.035(1)	102.002(7)	96.29(2)
γ (°)	90	90	88.73(2)
Vol. (\AA^3)	2012.38(7)	1593.2(2)	1024.1(5)
$D_{\rm calc} ({\rm Mg m}^{-3})$	1.374	1.501	1.350
Abs. coeff. (mm^{-1})	1.496	1.877	
F(000)	876	748	438
Radiation	MoK α ($\lambda = 0.71073$ Å)	MoK α (λ =0.71073 Å)	MoK α ($\lambda = 0.71073$ Å)
Temp. (K)	293(2)	293(2)	293(2)
θ range (°)	2.91-27.50	2.25-26.46	29.67-30.02
Limiting indices	$-10 \le h \le 10, \ 0 \le k \le 24,$	$0 \le h \le 11, \ 0 \le k \le 12$	$-10 \le h \le 10, 0 \le k \le 24$
	$0 \le l \le 17$	$-18 \le l \le 18$	$0 \le l \le 17$
No. unique reflections	4602	3129	3528
R	0.0548	0.0538	0.031
R _w	0.0391	0.0953	0.046
Goodness-of-fit on F^2	1.059	0.935	1.26
Largest diff. peak and hole	0.621 and -0.437 e A^{-3}	0.517 and -0.574 e A^{-3}	0.19 and -0.33 e A^{-3}

Table 3

Selected bond	distances	(Å)	and	bond	angles	(°)	of	$[Cu(R_2dtc)_2]$	
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Atoms	$[Cu_2(n-Pr_2dtc)_4]$	$[Cu_2(Et_2dtc)_4]$	$[Cu(i-Pr_2dtc)_2]$
Cu–S(1)	2.3161(11)	2.3071(9)	2.2912(7)
Cu-S(3)	2.3184(12)	2.299(1)	2.2912(7)
Cu−S(4)#1	2.7401(12)	2.844(1)	
Cu-S(2)	2.3166(11)	2.314(1)	2.2856(6)
Cu-S(4)	2.3221(11)	2.3270(9)	2.2856(6)
S(1) - C(1)	1.718(4)	1.718(3)	1.726(2)
S(3)–C(8)	1.707(4)	1.710(3)	1.715(2)
S(1)-Cu-S(2)	76.68(4)	77.00(3)	77.27(2)
S(3)-Cu-S(4)	76.25(4)	76.59(3)	76.73(2)
S(1)-Cu-S(4)	161.80(5)	102.20(3)	102.73(2)



Fig. 1. Molecular structure for $\text{Cu}_2(\text{Pr}_2\text{dtc})_4$ with the atomic numbering scheme.

expected, the axial Cu–S bond distance $\{2.740(1) \text{ Å in } [Cu_2(n-Pr_2dtc)_4]$, and 2.844(1) Å in $[Cu_2(Et_2dtc)_4]\}$ is longer than the equatorial Cu–S ones. The four basal sulfur atoms are coplanar but the Cu atom deviates from that plane showing a slight tetrahedral distortion. The bond length of Cu–S(4), 2.322(1) Å in $[Cu_2(n-Pr_2dtc)_4]$ and 2.3270(9) Å in $[Cu_2(Et_2dtc)_4]$, is the longest in Cu–S equatorial bond lengths because S(4) is a bridging atom. The bond angles of S(1)–Cu–S(2) and S(3)–Cu–S(4) are nearly the same $\{76.68(4)^\circ, 76.25(4)^\circ \text{ in } [Cu_2(n-Pr_2dtc)_4], and 77.00(3)^\circ, 76.59(3)^\circ \text{ in } [Cu_2(Et_2dtc)_4]\}.$

The bridging network Cu-S(4)-Cu#1-S(4)#1 is strictly planar owing to the inversion centre, with a $Cu\cdots$ Cu separation of 3.4179(6) Å in $[Cu_2(n-Pr_2dtc)_4]$, and 3.572(1) Å in $[Cu_2(Et_2dtc)_4]$. The Cu-S(4)-Cu#1-S(4)#1 and S(1)-S(2)-S(3)-S(4) planes are nearly perpendicular with a dihedral angle of 88.91(3)° in $[Cu_2(n-Pr_2dtc)_4]$. Our present results are in general accord with this earlier determination, although at a higher level of precision [22,23].

The structure of complex $[Cu(i-Pr_2dtc)_2]$ is built up of monomeric molecules. The two molecules, A and B, are crystallographically independent. Each Cu atom occupies a center of inversion, and, accordingly, the Cu and four S atoms are coplanar. The mean molecular planes of A and B are nearly perpendicular to each other, the dihedral angle being 89.3(2)°. The average of the four independent copper–sulfur distances is 2.2886(7) Å. The shortest copper–copper intermolecular distance is 7.629(1) Å. This



Fig. 2. A view of the crystal packing down the *a* axis for $Cu_2(Pr_2dtc)_4$.

redetermination confirms the main features of the earlier study [24,25].

To compare with the other copper(II) bis-(dialkyldithiocarbamate) complexes [22–26], we found that $[Cu_2(n-Pr_2dtc)_4]$ has the shortest Cu···Cu distance and $[Cu(i-Pr_2dtc)_2]$ has the longest one (Table 4). Also, the alkyl substituents at the nitrogen atom affect their coordination number and Cu–S distance (Table 4).

3.2. IR spectrum

Table 5 shows the most significant IR bands of the prepared compounds. The band in the range 1480–1510 cm⁻¹ is attributed to the v(C-N) stretching vibration [27], the band in the range 940–990 cm⁻¹, belonging to the v(C-S) stretching vibration [27,28], is considered indica-

Table 4	
Effect of different alkyl	substituents

tive of dithiocarbamate acting as a bidentate ligand [29]. As can be seen from Table 5, the effect of the substituents bonded at the nitrogen atom on the C-N and C-S bonds can be investigated. The lengthening of the alkyl chain is accompanied by a decrease of the v(C-N) band wavenumber; the lowest value is found for Cu(i-Pr₂dtc)₂, further lengthening of the chain does not lead to appreciable changes. The C-S bond lengths in derivatives involving different alkyl substituents are nearly equal; it can, therefore, be assumed that the electronic effects practically do not influence the v(C-S) vibrations. It is thus reasonable to attribute the lowering of the v(C-S) frequencies with the lengthening alkyl chain to the growing mass of the alkyl group, the irregularities in the wavenumbers being associated with their spatial arrangement. Nevertheless, it is necessary to note that the spectra of the Cu

Compound	$Cu(Me_2dtc)_2$	$Cu_2(Et_2dtc)_4^{a}$	$Cu_2(n-Pr_2dtc)_4$	$Cu(i-Pr_2dtc)_2^a$
Cu···Cu distance (Å)	4.043	3.572	3.418	7.629
Coordination number	6	5	5	4
Cu-S distance (Å)	2.3105	2.3117	2.3183	2.2886

^a Means data from crystal structure redetermined.

Table 5 Most significant IR bands (cm⁻¹) of Cu(R,dtc), complexes

-		-		
Compound	$Cu(Me_2dtc)_2$	$Cu_2(Et_2dtc)_4$	$Cu_2(n-Pr_2dtc)_4$	$Cu(i-Pr_2dtc)_2$
v(C–N)	1511s	1504s	1498s	1491s
v(C-S)	975s	913s, 997s	985s	940s

complexes, $[Cu_2(n-Pr_2dtc)_4]$ and $[Cu(i-Pr_2dtc)_2]$, for which the structure have been determined here using X-ray diffraction and which have a bidentate chelate and a bidentate bridged ligand, do not show any complexity in the zones of v(C-N) or v(C-S). For this reason it does not appear easy to decide from such IR data whether chelate or bridging dithiocarbamates are present.

3.3. EPR spectra and magnetic properties

The polycrystalline powder room-temperature EPR spectra for $[Cu(R_2dtc)_2]$ complexes are shown in Fig. 3. It may be seen from Fig. 3 that the shape and the parameters of the EPR spectra of (b) and (c) are very similar, which shows that there are the same coordination environments



Fig. 3. Room-temperature EPR spectra of the $[Cu(R_2dtc)_2]$ complexes.

between $[Cu(Et_2dtc)_2]$ and $[Cu(n-Pr_2dtc)_2]$. In addition, the half-field signal is not observed for (b) and (c) at room temperature, which suggests no magnetic interaction between the two Cu ions through the sulfur bridge. The values of $g_{\parallel} \ge g_{\perp} > 2.0$ of (a) and (b) suggested that the ground state was $d_{x^2-y^2}$ and the coordination geometry was octahedral or square-pyramidal [30,31]. The EPR spectrum of $[Cu(i-Pr_2dtc)_2]$ exhibited the expected four-line patterns, narrow linewidths characteristic of CuS_4 compounds [32]. The observation of g_{\parallel} and g_{\perp} indicates tetragonal distortion and supports the square-planar structure [15,23,33]. These results were consistent with the crystal structures.

The temperature dependence of the magnetic susceptibility per two copper atoms for the $[Cu(n-Pr_2dtc)_2]$ compound is shown in Fig. 4. The smooth decrease of χ_m with *T* in the range 300–75 K indicates that an antiferromagnetic interaction operates between the two copper atoms. With application of the Hamiltonian $H = -JS_1S_2$, the *J* values can be calculated from the modified Bleaney– Bower equation:

$$\chi_{\rm m} = 2N\beta^2 g^2 / KT [3 + \exp(-J/KT)] + 2N_{\alpha}$$

where J is the single-triplet (S-T) energy gap. The other symbols have their usual meaning. Assuming a constant value for N_{α} of 60×10^{-6} , the parameters J and g were determined by minimizing R described as $\Sigma(\chi_{\rm m}^{\rm obs} - \chi_{\rm m}^{\rm calc})^2 / \Sigma(\chi^{\rm obs})^2$, with J=44.93 cm⁻¹, g=2.032 and R= 1.88×10^{-4} .

3.4. Equilibrium studies

The equilibrium studies are taken in the EtOH solution by adding the ligands to the copper(II) compound. The intensity measurements were taken at the wavelength 435 nm, using the Meng–Jiang two-points formula [21]. The



Fig. 4. Experimental (\blacktriangle) and calculated (——) temperature dependence of $\chi_{\rm m}$ for [Cu(*n*-Pr₂dtc)₂].

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Table 6				
Stability co	nstants of [Cu(R	a_2 dtc) ₂] complexes	s in EtOH	solution

Compound	$Cu(Me_2dtc)_2$	$Cu_2(Et_2dtc)_4$	$Cu_2(n-Pr_2dtc)_4$	$Cu(i-Pr_2dtc)_2$
K _{eq}	3.03×10^{7}	6.85×10^{7}	6.29×10^{7}	1.40×10^{8}

equilibrium constants obtained are listed in Table 6. As can be seen in Table 6, the order of the stability of the difference alkyl groups in $[Cu(R_2dtc)_2]$ decreased as follows:

$$i$$
-Pr $>$ n-Pr \approx Et $>$ Me

This order due to the variety of alkyl groups may be partly attributed to changes in the residual positive charge and also partly to the steric hindrance of branched alkyl groups, but the electronic effects are rather more important than steric effects in this case. Also we found, when the $[Cu^{2+}]$ is surplus, there is a breakpoint in the absorption curve which suggests the formation of M:L=1:1 instability coordination complexes.

To compare with the solid state, the $[Cu(R_2dtc)_2]$ complexes in the solution have a similar change for a variety of alkyl groups. $[Cu(i-Pr_2dtc)_2]$ has the shortest Cu–S distance in the solid and the highest stability in the solution.

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