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Synthesis, spectral and single crystal X-ray structural studies on bis(2,2'-bipyridine)sulphidoM(II) (M = Cu or Zn) and diaqua 2,2'-bipyridine zinc(II)sulphate dihydrate

ARUMUGAM MANOHAR[1]*, KUPPUKANNU RAMALINGAM[2], GABRIELE BOCELLI[3] and ANDREA CANTONI[3]

[1]*Department of Chemistry, Kalasalingam University, Krishnankoil - 626 190,* [2]*Department of Chemistry, Annamalai Unviversity, Annamalainagar - 608 002, India and* [3]*Centro di studio per la strutturistica, Diffractometrica del CNR, Parma, Italy*

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Abstract: Reaction of bis(diethanoldithiocarbamato)copper(II), [Cu(deadtc)$_2$] and bis(di-*n*-propyldithiocarbamato)zinc(II), [Zn(dnpdtc)$_2$] complexes with 2,2'-bipyridine (2,2'-bipy) (1:1 ratio) in ethanol was investigated. Simple mixing of the reactants in 1:1 ratio resulted in five-coordinated [Cu(2,2'-bipy)$_2$S]·$CH_3CH_2OSO_3H$ (**1**) and [Zn(2,2'-bipy)$_2$S]·$CH_3CH_2OSO_3H \cdot 2H_2O$ (**2**). Refluxing the reactants and cooling the contents result in the formation of [Zn(2,2'-bipy)(H_2O)$_2$]SO_4 (**3**) and [Cu(2,2'-bipy)(H_2O)$_2$]SO_4 (**4**). Complexes **1** and **2** are monomeric with trigonal bipyramidal geometry. A distorted octahedral environment was observed in complexes **3** and **4**. The crystal structure of **4** has already been reported in the literature. Crystal structures of **1**, **2** and **3** are reported in this paper. The M–S distances in **1** and **2** are 2.318(1) Å and 2.323 Å, respectively. The N–M–S angles are larger than the N–M–N angles due to the steric requirements.

Keywords: dithiocarbamates; 2,2'-bipyridine; tbp geometry; single crystal X-ray.

INTRODUCTION

Bisdithiocarbamate complexes have been investigated extensively.[1,2] The interaction of metal dithiocarbamates with Lewis bases leads to the formation of the corresponding base adducts.[3–7] Bis(dialkyldithiocarbamato)nickel(II) complexes, [Ni(dtc)$_2$] show interesting variations in their reactions with Lewis bases.[8–12] Bis(diethyldithiocarbamato)nickel(II) was shown to form an adduct with pyridine only at liquid nitrogen temperature, whereas similar complexes with electron withdrawing substituents on the dithiocarbamate moiety formed an adduct with ease at ambient temperature.[13] Other than the adduct formation reac-

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* Corresponding author. E-mail: navmanohar@yahoo.co.in
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tion, similar complexes were shown to also promote redox reactions of the ligands under basic conditions. A copperthiol complex [Cu(RSH)$_2$Cl] in pyridine was shown to oxidize thioamides, thiols, sulphide ion and sulphur to sulphate ion.[14] Transition metal ions, such as copper(II), iron(II) and nickel(II), are known to promote oxidation of sulphur compounds under basic conditions.[15] One such instance is the oxidation of sulphides, thioamides and sulphur to SO_4^{2-} by the copper(II)/pyridine system. A new mononuclear copper(II) complex, [CuCl(2,2'-bipy)$_2$]BF$_4$·CH$_2$Cl$_2$, was reported and its X-ray analysis revealed a slightly distorted trigonal-bipyramidal coordination geometry of copper(II).[16] The crystal structure of [Zn(5,5'-Me$_2$-2,2'-bipy)(H$_2$O)$_4$]SO$_4$ was reported recently.[17] The Zn(II) complex cation, with approximate twofold symmetry, displayed a slightly distorted octahedral geometry around the Zn(II) atom, which was coordinated by two N atoms from the 5,5'-dimethyl-2,2'-bipyridine ligand and by the O atoms of four water molecules. Reaction of bis(diethanoldithiocarbamato)nickel(II) with ethylenediamine produced [Ni(en)$_3$]S$_2$O$_3$.[18] Oxidation of dithiocarbamate to thiosulphate in basic medium was established. In continuation of our interest in such reactivity studies, bis(diethanoldithiocarbamato)copper(II), [Cu(deadtc)$_2$] and bis(di-*n*-propyl dithiocarbamato)zinc(II), [Zn(dnpdtc)$_2$] complexes were allowed to react with 2,2'-bpy (1:2 ratio) in ethanol. The products were analysed and structurally investigated and the results are reported herein.

EXPERIMENTAL

Materials

Diethanolamine (99 %), di-*n*-propylamine (97 %), CS$_2$ (95 %), copper(II) chloride dihydrate (95 %), zinc(II) sulphate heptahydrate (97 %) and 2,2'-bipyridine (97 %) were obtained from Merck. Ethanol was of HPLC grade.

Preparation

The parent Cu(deadtc)$_2$ and Zn(dnpdtc)$_2$ complexes were prepared by literature methods.[1,2]

i) Ethanolic solutions of Cu(deadtc)$_2$ (10 mmol, 423 mg, 25 cm^3 ethanol) and 2,2'-bipyridine (20 mmol, 312 mg, 25 cm^3 ethanol) were thoroughly mixed and then left undisturbed. The solutions turned bluish green overnight and light blue crystals separated from the solution after about seven days. The crystals analysed to the formula [Cu(2,2'-bipy)$_2$S]CH$_3$CH$_2$OSO$_3$H (**1**). Yield: 80 %; Anal. Calcd. for C$_{22}$H$_{22}$N$_4$O$_4$S$_2$Cu: C, 49.4; H, 4.1; N, 10.5 %. Found: C, 49.3; H, 4.0; N, 10.3 %; UV-Vis (ethanol) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 750 (100), 365 (14400).

ii) A similar procedure as described above was followed with Zn(dnpdtc)$_2$ in ethanol. Pale yellow crystals separated from the solution. The crystals analysed to the formula [Zn(2,2'-bipy)$_2$S]CH$_3$CH$_2$OSO$_3$H·2H$_2$O (**2**). Yield: 80 %; Anal. Calcd. for C$_{22}$H$_{26}$N$_4$O$_6$S$_2$Zn: C. 46.1; H, 4.6; N, 9.8 %. Found: C, 46.0; H, 4.5; N, 9.6 %; UV–Vis (ethanol) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 320 (15700).

iii) Ethanolic solution 2,2'-bipyridine (20 mmol, 312 mg, 25cm^3 ethanol) and Zn(dnpdtc)$_2$ (10 mmol, 417 mg, 25 cm^3 ethanol) were thoroughly mixed with continuous stirring and the resulting solution was refluxed for one hour and then allowed to cool. Dirty colourless crystals were obtained which analysed to [Zn(2,2’-bipy)(H_2O)$_2$]SO_4 (**3**). Yield: 75%. Anal. Calcd. for $C_{10}H_{12}N_2O_6SZn$: C, 33.9; H, 3.4; N, 7.9 %. Found: C, 33.8; H, 3.2; N, 7.8 %. UV–Vis (ethanol) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 325(15200).

iv) A similar procedure as described for compound **3** was followed with Cu(deadtc)$_2$ of ethanol. Pale blue crystals were obtained which analysed to [Cu(2,2’-bipy)(H_2O)$_2$]SO_4 (**4**). Yield: 75%. Anal. Calcd. for $C_{10}H_{12}N_2O_6SCu$: C, 34.2; H, 3.4; N, 7.9 %. Found: C, 34.1; H, 3.2; N, 7.7 %. UV–Vis (ethanol) (λ_{max} / nm (ε / L mol^{-1} cm^{-1})): 745(100), 360(14200).

Analytical and physical measurements

UV-Visible spectra were recorded on a Jasco Uvdec-650 spectrometer and the IR spectra were recorded as KBr pellets using a Jasco IR-100 spectrometer. Elemental analyses (C, H, N) were realised with a Heraeus Carlo Erba 1108 instrument.

X-Ray crystallography

Details of crystal data, data collection and refinement parameters for complexes **1**–**4** are summarized in Table I. Selected bond distances and angles are given in Table II. The intensity data were collected at room temperature (298 K) on a Philips PW100 single crystal diffractometer using Mo-Kα radiation (0.71060 Å) for compound **1**. A Siemens AED and an Enraf Nonius CAD4 diffractometer were used for compounds **2** and **3,** respectively, employing Cu-Kα radiation (1.541780 Å) for data collection. For compound **1**, the structure was solved by the Shelxl 92 program and refined by Shelx 93.[19] Structures **2** and **3** were solved by using the SIR92[20] program and refined using Shelx 93.[19] All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically.

RESULTS AND DISCUSSION

Electronic spectra and IR spectra

The electronic spectra of both copper complexes showed a prominent band around 750 nm. Another band around 365 nm observed for compound **1** was more intense indicating a charge transfer transition. However, the zinc complexes showed only a strong charge transfer band around 320 nm. The IR spectra of all four complexes showed strong absorptions due to ν(O–H), other than ring ν(C–N) vibrations in the range 1590 cm^{-1}, as observed before.[21]

X-Ray structures

Molecular diagrams of complexes are given in Figs. 1–3. Complexes **1** and **2**, and **3** and **4** are isostructural. Although the crystal structure of complex **4** has already been reported in the literature,[22] the compound was prepared by a direct procedure involving the reactants. In this investigation, complex **4** was obtained from reactivity studies. Therefore, only the crystal structures of three complexes, *viz.*, **1**–**3**, are reported in this paper.

Complex **1** displays a distorted trigonal bipyramidal geometry around the Cu(II) atom, which is coordinated by four N atoms from a 2,2’-bipyridine ligand and by the S atom. Two sets of Cu–N distances were observed. The axial distances are short compared to the equatorial ones. The axial Cu–N distances are 1.988(2) and 1.991(2) Å and the equatorial distances are 2.105(2) and 2.109(2) Å.

TABLE I. Crystal data, data collection and refinement parameters for the complexes **1**–**4**

Parameter	**1**	**2**	**3**	**4**
Empirical formula	$C_{22}H_{22}N_4O_4S_2Cu$	$C_{22}H_{26}N_4O_6S_2Zn$	$C_{10}H_{12}N_2O_6SZn$	$C_{10}H_{12}N_2O_6SCu$
FW	535.1	573.0	353.7	351.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	I2/a	I2/a
a / Å	27.130(3)	27.104(2)	6.990(3)	7.010(3)
b / Å	7.782(3)	7.787(3)	12.466(3)	12.488(3)
c / Å	23.697(2)	23.650(3)	14.867(3)	14.883(2)
α / °	90	90	90	90
β / °	97.99(4)	97.97(3)	101.11(3)	101.12(4)
γ / °	90	90	90	90
U / Å^3	4954.48(2)	4943.33(2)	1272.83	1278.4
Z	8	8	4	4
Dc / g cm^{-3}	1.4346	1.5396	1.504	1.8070
μ / cm^{-1}	10.879	33.345	30.474	18.929
F(000)	2352	2360	2512	2392
λ / Å	Mo-Kα (0.71069)	Cu-Kα (1.54178)	Cu-Kα (1.54178)	Mo-Kα (0.71069)
θ range, ° (scan type ω-2θ)	3–30	3–70	3–70	3–30
Index ranges	$-38 \le h \le 37, 0 \le k \le 10, 0 \le l \le 33$	$-32 \le h \le 32, 0 \le k \le 9, 0 \le l \le 28$	$-7 \le h \le 8, 0 \le k \le 15, 0 \le l \le 18$	$-4 \le h \le 8, -14 \le k \le 15, -19 \le l \le 18$
Reflections collected	7199	10344	2661	1395
Observed reflections	4516	4329	1201	937
Weighting scheme	$w = 1/(\sigma^2(Fo)^2 +$	$w = 1/(\sigma^2(Fo)^2 +$	$w = 1/(\sigma^2(Fo)^2 +$	$w = 1/(\sigma^2(Fo)^2 + (0.0645P)^2$
$P = \max(Fo^2 + 2Fc^2)/3$	$+ (0.0356P)^2 + 0.0000P)$	$+ (0.1709P)^2 + 2.27P)$	$+ (0.0606P)^2 + 6.91P)$	$+ 0.000P)$
Number of parameters refined	417	417	409	109
Final R, R_w (obs. data)	0.0469, 0.0842	0.0522, 0.1941	0.0515, 0.1497	0.0377, 0.0917
GOOF	0.998	1.037	1.392	0.927

TABLE II. Selected bond distances and angles

Compound **1**		Compound **2**		Compound **3**	
Distances, Å					
Cu–S2	2.318(1)	Zn–S2	2.323(1)	Zn–O4	2.451 (3)
Cu–N3	1.991(2)	Zn–N3	2.101(2)	Zn–N6	1.992(2)
Cu–N14	2.109(2)	Zn–N14	1.980(2)	S2–O4	1.462(2)
Cu–N15	2.105(2)	Zn–N26	2.111(3)	S2–O5	1.489(2)
Cu–N26	1.988(2)	N3–C4	1.334(4)	N6–C7	1.339(5)
N3–C4	1.343(4)	N3–C8	1.355(3)	N6–C11	1.355(4)
N3–C8	1.344(3)	C4–C5	1.396(5)	Zn–O3	2.033(2)
C4–C5	1.376	C9–N14	1.346(4)	C7–C8	1.350(7)
C9–N14	1.353(3)	C13–N14	1.344(4)	C8–C9	1.368(6)
C13–N14	1.337(4)	N15–C16	1.333(4)	C10–C11	1.392(5)
N15–C16	1.341(4)	Zn–N15	1.980(2)		
Angles, °					
N15–Cu–N26	79.9(1)	N15–Zn–N26	79.8(1)	C8–C9–C10	119.71(2)
N14–Cu–N26	96.5(1)	N14–Zn–N26	96.6(1)	C9–C10–C11	117.81(2)
N14–Cu–N15	113.5(1)	N14–Zn–N15	174.5(1)	N6–C11–C10	121.71(2)
N3–Cu–N26	174.5(1)	N3–Zn–N26	113.5(1)	N6–C7–C8	123.5(4)
N3–Cu–N15	97.9(0)	N3–Zn–N15	97.8(0)	O4–S2–O5	108.4(2)
N3–Cu–N14	79.6(1)	N3–Zn–N14	79.7(1)	Zn–O4–S2	133.1(2)
S2–Cu–N26	92.8(0)	S2–Zn–N26	120.7(0)	C7–N6–C11	118.1(3)
S2–Cu–N15	125.9(0)	S2–Zn–N15	92.4(0)	C7–C8–C9	119.2(4)
S2–Cu–N14	120.5(0)	S2–Zn–N14	93.0(0)		
S2–Cu–N3	92.5(0)	S2–Zn–N3	126.0(0)		

Interestingly, the Cu–S distance is 2.318(1) Å. This is in keeping with the distances observed in similar Cu(2,2'-bpy)$_2$X complexes, where X = $S_2O_3^{2-}$ and $S_4O_6^{2-}$ and the corresponding distances are 2.367 and 2.672 Å, respectively.[23,24] The heteroatom lies in the equatorial plane in all the cases, as observed in the present case also. The heteroatom because of its bulkiness shows a distortion and hence the N–Cu–N angle is 113.5(1)° whereas the N–Cu–S angles are 120.5(0)° and 125.9(0)°.

Complex **2** is also monomeric with a trigonal bipyramidal geometry. The heteroatom 'S' is in the equatorial plane with a Zn–S distance of 2.323(1) Å. Two sets of Zn–N distances, as in **1**, were observed, with those in equatorial position, *viz*., 2.101(3) and 2.111(3) Å, being longer than those in axial positions, *viz*., 1.980(2) and 1.980(2) Å. In addition, the N–Zn–N angle is smaller (113.3(1)°) than the larger two, *viz*., 120.7(0) and 126.0(0)°. The observed angles are close to those reported for [Zn(2,2'-bpy)$_2$(ONO)]NO_3.[25] Both structures **1** and **2** are similar and a molecule of $CH_3CH_2OSO_3H$ co-crystallized with them. The bond parameters associated with the bipyridine rings are normal.

Complex **3** has a ZnN_2O_4 coordination environment with SO_4^{2-} acting as bridging ligand between two zinc ions, as observed in the case of the already reported copper analogue.[22] The largest Zn–O distance with sulphate ion is 2.451(3)

Å. The Zn–N distances are 1.992(2) Å and 1.993(2) Å. A distorted octahedral environment around zinc was observed.

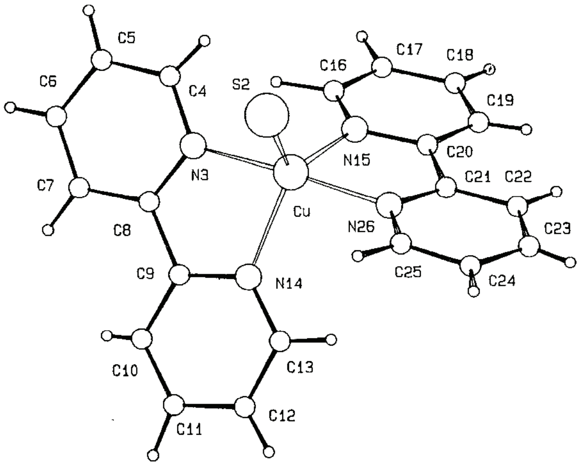

Fig. 1. Molecular structure of [Cu(2,2'-bpy)$_2$S]·$CH_3CH_2OSO_3H$; ($CH_3CH_2OSO_3H$ is omitted from the diagram).

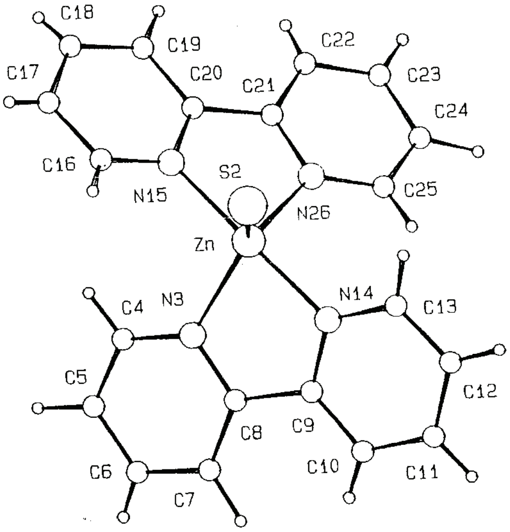

Fig. 2. Molecular structure of [Zn(2,2'-bpy)$_2$S]·$CH_3CH_2OSO_3H \cdot 2H_2O$; ($CH_3CH_2OSO_3H \cdot 2H_2O$ is omitted from the diagram).

The crystallographic data for the structures are deposited at the Cambridge Crystallographic Data Centre, under deposition numbers: CCDC 163525, CCDC 163526, CCDC 163527. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: intcode+(1223)336 033; e-mail: teched@chemcrys.cam.ac.uk).

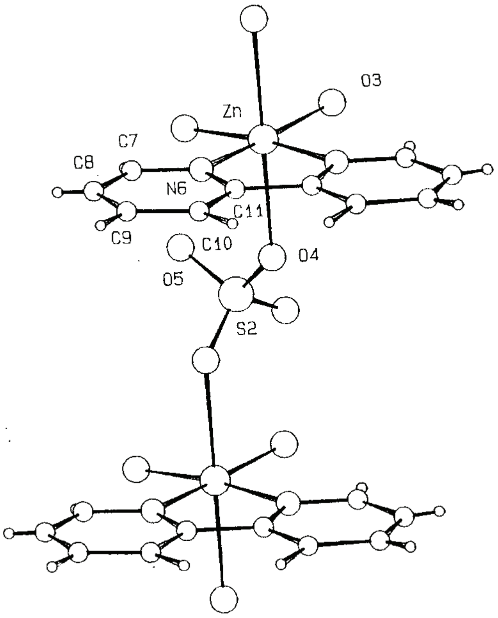

Fig. 3. Molecular structure of [Zn(2,2'-bpy)$(H_2O)_2$]SO_4.

CONCLUSIONS

Reaction of [Cu(deadtc)$_2$] and [Zn(dnpdtc)$_2$] with 2,2'-bipyridine produced the complexes **1**–**4** at room temperature and under refluxing conditions, respectively. The crystal structures of the complexes **1**–**3** are reported in this paper. Complexes **1** and **2** have trigonal bipyramidal geometry, while a distorted octahedral environment was observed in complexes **3** and **4**. This paper reports the oxidation of the dithiocarbamate ligand to a sulphate anion. Conversion to $CH_3CH_2OSO_3H$ was observed at room temperature. However, under refluxing conditions, complete conversion to SO_4^{2-} was observed. Sulphide ion coordination was observed on rare occasions leading to the formation of the five-coordinated MN_4S (M = Cu or Zn) chromophore. Although, a similar conversion of dithiocarbamate to $S_2O_3^{2-}$ in ethylenediamine was reported, this paper reports the first instance of oxidation of dithiocarbamate to SO_4^{2-}.

ИЗВОД

СИНТЕЗА, СПЕКТРАЛНА И РЕНДГЕНСКА СТРУКТУРНА ПРОУЧАВАЊА НА МОНОКРИСТАЛУ БИС(2,2'-БИПИРИДИН)СУЛФИДО-М(II) (M = Cu ИЛИ Zn) И ДИАКВА-2,2'-БИПИРИДИН-ЦИНК(II)-СУЛФАТА ДИХИДРАТА

ARUMUGAM MANOHAR[1], KUPPUKANNU RAMALINGAM[2], GABRIELE BOCELLI[3] и ANDREA CANTONI[3]

[1]*Department of Chemistry, Kalasalingam University, Krishnankoil – 626 190,* [2]*Department of Chemistry, Annamalai Unviversity, Annamalainagar – 608 002, India и* [3]*Centro di studio per la strutturistica, Diffractometrica del CNR, Parma, Italy*

Изучавана је реакција комплекса бис(диетанолдитиокарбамато)бакра(II), [Cu(deadtc)$_2$] и бис(ди-*n*-пропилдитиокарбамато)цинка(II), [Zn(dnpdtc)$_2$] са 2,2'-бипиридином (2,2'-bipy) (у

односу 1:1) у етанолу. Једноставним мешањем реактаната у односу 1:1 даје петокоординатне [Cu(2,2'-bipy)$_2$S]·$CH_3CH_2OSO_3H$ (**1**), [Zn(2,2'-bipy)$_2$S]·$CH_3CH_2OSO_3H.2H_2O$ (**2**). Рефлуктовањем реактаната и хлађењем садржаја добијају се [Zn(2,2'-bipy)(H_2O)$_2$]SO_4 (**3**) и [Cu(2,2'-bipy)(H_2O)$_2$]SO_4 (**4**). Комплекси **1** и **2** су мономерни са тригонално-бипирамидалном геометријом. Дисторгована октаедарска околина је примећена у комплексима **3** и **4**. Кристална структура **4** је већ објављена у литератури. кристалне структуре **1**, **2** и **3** су објављене у овом раду. M–S растојања у **1** и **2** су 2.318(1) Å односно 2.323 Å. N–M–S углови су већи од углова N–M–N из стерних разлога.

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