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A new family of pyrazolyl-based anionic bidentate ligands and crystal structure of bis(*N*-phenyl-2-pyrazolyl-1-carboximidothioato)copper(II)

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Abstract

Three new N,S-donor bidentate pyrazolyl-based ligands abbreviated as $[PhNCSPz]^-$, **1**, $[PhNCSPz^{Me2}]^-$, **2**, and $[PhNCSPz^{Ph2}]^-$, **3**, have been synthesized in THF by direct mixing of phenylisothiocyanide with suspension of appropriate sodium-pyrazolate salts and characterized by the common spectroscopic and analytical methods. The Cu(II) complexes of these anionic chelate ligands have been characterized and the crystal structure of $Cu(PhNCSPz)_2$, **4**, has been determined. The space group of complex is $P2_1c$, with $a = 5.9313(3)$, $b = 21.206(1)$ Å, $c = 8.0667(4)$ Å, $\beta = 103.822(1)°$.

Keywords: Pyrazolyl-based ligands; Polypyrazolylborate; Copper complexes; Model compounds

1. Introduction

There are a lot of publications on coordination chemistry of pyrazole-based chelating ligands which present versatile coordination geometry and nuclearity [1]. The suitable structure and high stability of pyrazoles, in addition to the ability of their deprotonated form to act as powerful nucleophiles in substitution reactions, have made them as good candidates for incorporation in the design of new ligands. The easy control of the electronic and steric properties of the pyrazolyl-derived ligands by introducing different substituents in the pyrazolyl rings is another advantage and expands the domain of pyrazole-type ligands. Pyrazoles also can behave as *endo*- or *exo*-bidentate bridging ligands in the form of pyrazolato anion [2–7]. The realm of pyrazolyl-based ligands, similar to those of the well known classical polypyrazolylborate congeners, is completely fertile and wide and their complexes may exhibit interesting roles such as catalysts, models, pharmaceuticals, etc. [8–15].

Recently we have reported some copper(I) complexes containing tetrathiometallate and polypyrazolylborate ligands, providing N_2S_2 coordination environment around copper atoms. In sight of structural and spectroscopic similarities between our complexes and active sites of copper proteins, we introduced them as model compounds [16–18]. As a result of high tendency of anionic S-donor ligands, specially tetrathiomolybdate or tetrathiotangustate, to reduce Cu(II) to Cu(I) [19], our try to synthesis Cu(II) complexes containing tetrathiometallate and polypyrazolylborate ligands was led to failure. In fact, complexes containing Cu(II)–S bonds show a tendency to undergo redox reactions which normally converts Cu(II) to Cu(I) [20]. Particularly, Cu(II)–

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thiolate complexes containing N-donors from pyrazolyl-derived ligands are rare and according to our knowledge, the compound [Cu(HB(3,5-*i*Pr$_2$Pz)$_3$)(SCPh$_3$)] is the only structurally characterized example [21]. Continuing our interest to copper complexes containing N_2S_2 chromophors, herein we report the novel N,S-donor bidentate ligands **1**–**3** (Fig. 1) and their Cu(II) complexes, **4**–**6**. The compound **4** is monomeric and the co-ordination environment around copper(II) atom is *trans*-N_2S_2 forming a perfect square planar geometry (Fig. 2).

2. Experimental

2.1. General considerations

All operations were carried out under a pure dinitrogen or argon atmosphere using Schlenk techniques. All reagents and solvents were purchased from commercial sources and the solvents were dried by standard procedure [22] and were degassed by three freeze-pump-thaw cycles. ^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX500 AVANCE spectrometer. Peaks were assigned on the basis of chemical shift, integration, and coupling patterns. IR spectra were recorded on a FT BRUKER or SHIMADZU IR-470 infrared spectrophotometers using pressed KBr disks with polystyrene as reference. UV–Vis spectra were obtained on a JASCO model 7850 spectrophotometer.

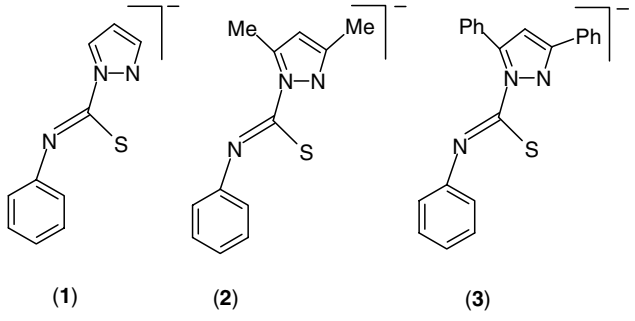

Fig. 1. Pyrazolyl-based ligands PzRS$^-$, **1**, Pz^{Me2}RS$^-$, **2**, and Pz^{Ph2}RS$^-$, **3**, (R = PhNC).

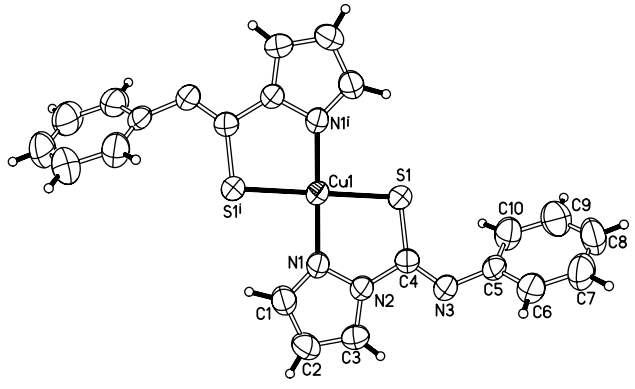

Fig. 2. Structure of the [Cu(PhNCSPz)$_2$], **4**, showing the numbering scheme.

2.2. Synthesis of Na[PhNCSPz] (*1*)

A solution of pyrazole (0.68 g, 10 mmol) in 25 ml dry THF was treated with solid NaH (55%, 0.44 g, 10 mmol) under Ar atmosphere. After stirring for 3 h, PhNCS (1.2 ml (d = 1.13 g/ml), 10 mmol) was added into the resulting suspension of NaPz and the reaction was continued overnight at r.t. The suspension was filtered using a fritted funnel and the collected white solid (PhNCSPz) washed with cold THF (2 × 10 ml) and *n*-hexane (2 × 25 ml) and dried in vacuo (2.13 g, 95%); m.p. = 250 °C (commence of melting along with color change and decomposition). IR (KBr, cm^{-1}): 3127w broad, ν(C–H), 1595s, 1557vs, 1509s, 1446w, 1388s, 1315m, 1241vs, 1187s, 1170w, 1089s, 1043s, 986s, 931s, 915w, 904w, 767s, 704s, 632m. ^{1}H NMR (DMSO-d_6, δ ppm, J Hz): 6.26 (dd, $^3J_{H-H}$ = 3 and 5, 1H, 4-H in Pz), 6.88 (tt, J_{H-H} = 3 and 19, 1H, 4-H in Ph), 7.01 (d, $^3J_{H-H}$ = 3, 1H, 3-H or 5-H in Pz), 7.04 (d, $^3J_{H-H}$ = 5, 1H, 3-H or 5-H in Pz), 7.21 (t, J_{H-H} = 19.0, 3H, in Ph), 7.43 (t, J_{H-H} = 3, 1H, in Ph); ^{13}C NMR (DMSO-d_6, δ): 104.66, 120.64, 121.66, 122.95, 127.39, 127.57, 130.41, 139.39, 153.10, 167.71. Anal. Calc. for $C_{10}H_8N_3NaS$: C, 53.33; H, 3.56; N, 18.67; S, 14.22. Found: C, 52.83; H, 3.40; N, 19.17; S, 14.10%.

2.3. Synthesis of Na[PhNCSPz^{Me2}] (*2*)

PhNCS (1.2 ml, 10 mmol) was added to a stirred suspension of Na(3,5-Me$_2$Pz) (1.18 g, 10 mmol) in THF (40 ml). After being refluxed for 6 h, the suspension was cooled to r.t. and filtered using a fritted funnel and the collected white solid Na[PhNCSPz^{Me2}] was washed with cold THF (2 × ml) and *n*-hexane (2 × 25 ml) and dried in vacuo (2.22 g, 88%); m.p. = 300 °C (commence of melting along with color change and decomposition). IR (KBr, cm^{-1}): 1634m, 1606m, 1498s, 1476m, 1447m, 1384s, 1322m, 1135m (b), 999vs, 829w, 689s, 656m, 546m (b), 473m. ^{1}H NMR (DMSO-d_6, δ ppm, J Hz): 2.11 (b, 3H, CH$_3$ in 3,5-(CH$_3$)$_2$Pz). 2.39 (b, 3H, CH$_3$ in 3,5-(CH$_3$)$_2$Pz), 6.25 (t, $^3J_{N-H}$ = 4, 1H, 4-H in 3,5-(CH$_3$)$_2$Pz), 6.85 (t, $^3J_{H-H}$ = 19, 1H, 4-H in Ph), 7.00 (d, J_{H-H} = 18.0, 2H, 2-H and 6-H in Ph), 7.19 (t, 2 H, 3-H and 5-H in Ph). Anal. Calc. for $C_{12}H_{12}N_3NaS$: C, 56.92; H, 4.74; N, 16.6; S, 12.65. Found: C, 57.41; H, 4.69; N, 16.2; S, 12.51%.

2.4. Synthesis of Na[PhNCSPz^{Ph2}] (*3*)

PhNCS (1.2 ml, 10 mmol) was added to a stirred suspension of Na(3,5-Ph$_2$Pz) (2.42 g, 10 mmol) in THF (60 ml). After being refluxed for 8 h, the suspension was

cooled to r.t. and filtered using a fritted funnel and the collected white solid Na[PhNCSPz^{Ph2}] was washed with cold THF (2 × 1 ml) and *n*-hexane (2 × 25 ml) and dried in vacuo (2.94 g, 78%); m.p. = 350 °C (commence of melting along with color change and decomposition). IR (KBr, cm^{-1}): 2800–3400s (broad multipet), *ν*(C–H), 15991w, 1541m, 1496s, 1461s, 1384s, 1344w, 1316w, 1295w, 1272w, 1075m, 1057w, 976s, 916w, 754vs, 698s, 688s. ^{1}H NMR (DMSO-d_6, δ): 7.02 (t, J = 20, 1H, 4-H in PhNCS), 7.19 (s, 1H, 4-H in Pz), 7.25 (t, J = 20, 2H, 3-H and 5-H in PhNCS), 7.34 (t, J = 19, 2H, 4-H in PhPz), 7.45 (t, J = 19, 4H, 3-H and 5-H in PhPz), 7.57 (d, J = 20, 2H, 2-H and 6-H in PhNCS), 7.84 (d, J = 19, 4H, 2H, 2-H and 6-H in PhPz). ^{13}C NMR (DMSO-d_6, δ): 99.617, 123.14, 123.91, 125.10, 127.79, 127.97, 127.82, 131.47, 138.42, 149.88, 168.21. Anal. Calc. for $C_{22}H_{16}N_3NaS$: C, 70.03; H, 4.24; N, 11.14; S, 8.49. Found: C, 70.45; H, 4.32; N, 11.03; S, 8.61%.

2.5. Synthesis of CuL_2, L = [PhNCSPz]$^-$ (4)

Solid Na[PhNCSPz] (0.45 g, 2.0 mmol) and $CuBr_2$ (0.22 g, 1 mmol) were added into acetone (30 ml) and stirred for 4 h. The resulting deep violet solution was filtered and the solvent removed in vacuo (yield 0.42 g, 90%): IR (KBr, cm^{-1}): 3132w and 3120w, *ν*(C–H), 1593vs, 1500w, 1460w, 1431s, 1391m, 1339m, 1278m, 1216m, 1201m, 1102m, 1073s, 942vs, 910m, 780s, 763m, 693s, 609m. Electronic spectrum (DMF, nm, absorbance): 320 (1.52), 290 (sh), 266 (1.83), 256 (1.34). Anal. Calc. for $C_{20}H_{16}CuN_6S_2$: C, 51.34; H, 3.42; N, 17.97; S, 13.69. Found: C, 51.01; H, 3.52; N, 18.10; S, 13.44%.

2.6. Synthesis of CuL_2, L = [PhNCSPz^{Me2}]$^-$ (5)

A mixture of Na[PhNCSPz^{Me2}] (0.51 g, 2.0 mmol) and $CuBr_2$ (0.22 g, 1 mmol) was stirred in acetone (40 ml) for 6 h. The precipitated NaBr was separated by filtration and the filtrate was dried in vacuo (yield 0.45 g, 87%): IR (KBr, cm^{-1}): 2900–3100w (multipletes), *ν*(C–H), 1607vs, 1590vs, 1486w, 1467w, 1415m, s, 1380w, 1347s, 1336s, 1269w, 1206s, 1054m, 991w, 940s, 811m, 794w, 769m, 756m, 698s. Electronic spectrum (DMF, λ nm, absorbance): 426 (0.25), 312 (1.40), 267 (2.0), 258 (1.35). Anal. Calc. for $C_{24}H_{24}CuN_6S_2$: C, 55.01; H, 4.58; N, 16.05; S, 12.22. Found: C, 54.91; H, 4.63; N, 16.25; S, 12.00%.

2.7. Synthesis of CuL_2, L = [PhNCSPz^{Ph2}]$^-$ (6)

A mixture of Na[PhNCSPz^{Me2}] (0.38 g, 1.0 mmol) and $CuBr_2$ (0.11 g, 0.5 mmol) was refluxed in acetone (40 ml) for 8 h. The precipitated NaBr was separated by filtration and the filtrate was dried in vacuo (yield 0.31 g, 80%): IR (KBr, cm^{-1}): 2863–3136b (multipletes), *ν*(C–H), 1659w, 1635w, 1601w, 1568w, 1494m, 1462s, 1447m, 1272w, 916m, 753vs, 688vs. Electronic spectrum (DMF, λ nm, absorbance): 281 (2). Anal. Calc. for $C_{44}H_{32}CuN_6S_2$: C, 68.44; H, 4.15; N, 10.89; S, 8.04. Found: C, 68.66; H, 4.07; N, 11.01; S, 7.95%.

2.8. X-ray crystallography

Diffraction studies of the complex **4** were performed on a Bruker 2001 SMART CCD diffractometer. Mo Kα radiation (λ = 0.71073 Å) was employed for data collection at 113 K. Crystal data, structure solution and refinement for **4** are summarized in Table 1.

3. Result and discussion

3.1. Ligand synthesis

The ligands **1**–**3** were readily prepared in THF from the reactions of equimolar amounts of phenylisothiocyanide and the corresponding sodium pyrazolates Na(3,5-R$_2$Pz), as illustrated in the following equation:

$$NaPz^{R2} + PhNCS \rightarrow Na^+[PhNCSPz^{R2}]^- \quad (R = H, Me, Ph) \tag{1}$$

Deprotonation of pyrazoles to form the NaPz^{R2}, can be facilitated by application of an alkali or a base (typically, triethylamine) or by means of interaction of pyrazole with *n*-butyllithium, pyrazole with an alkali metal in THF, or pyrazole with an alkali metal hydride [2]. The salts **1**–**3** were isolated in high yield (78–95%) as white powders after separating by filtration and subsequent washing with cold THF and *n*-hexane. They are stable in dry air for months and show sufficient solubility in

Table 1
Crystallographic data for compound **1**

Chemical formula	$C_{20}H_{16}CuN_6S_2$
Formula weight	467.5
Crystal system, space group	$P2_1/c$
Unit cell dimensions	
a (Å)	5.9313(3)
b (Å)	21.206(1)
c (Å)	8.0667(4)
β (°)	103.822(1)
V (Å^3)	985.22(8)
Z	2
D_{calc} (g cm^{-3})	1.578
μ (mm^{-1})	1.340
Crystal size (mm)	0.59 × 0.22 × 0.18
θ_{max} (°)	26.4
Reflections collected	8176
Independent reflections	1999
Parameters	133
R [$I > 2\sigma$]	0.026
R_w (all data)	0.031
Goodness-of-fit on F^2	1.05
Electron density extremes (e Å^{-3})	−0.38 to 0.19

common solvents such as dichloromethane, acetone or tetrahydrofuran. The formation of the ligands from reactants can be easily controlled by solid state IR spectroscopy: the absence of –SCN pick at the region 2000–2100 cm^{-1} along with the appearance of some new bands other than those of corresponding pyrazolates, clearly verifies the production of the ligands. It is also important to note that we have successfully used a similar method to prepare other new bidentate ligands such as $Na^+[PhNCSBtz]^-$ (Btz = benzotriazole) or $Na^+[PhNCSImz]^-$ (Imz = imidazole) from the reactions of PhNCS and NaBtz or NaImz, respectively, an observation that illustrates the general applicability of our methodology. The contribution of PhNCS in preparation of new N,S-donor ligands has also been reported by Shen and Yao [23] and they have been considered the activation of PhNCS by organolanthanoid complexes as driving force of reaction.

3.2. Preparation of copper complexes

The complexes **4**–**6** were prepared in acetone or tetrahydrofuran through one-pot reaction by mixing of the corresponding ligands with $CuBr_2$ in 2:1 molar ratio, in nearly quantitative yield (Eq. (2)), even though, synthesis of the complexes by the self assembly method via direct mixing of reactants was also successful (Eq. (3))

$$2Na[PhNCSPz^{R2}] + CuBr_2 \rightarrow CuL_2 + 2NaBr \quad (L = [PhNCSPz^{R2}]) \qquad (2)$$

$$2Pz^{R2} + 2PhNCS + CuCl \rightarrow CuL_2 + 2HCl \quad (L = [PhNCSPz^{R2}]) \qquad (3)$$

All compounds **4**–**6** are completely air stable and **4** and **5** is highly but **6** slightly soluble in most of laboratory solvents such as acetone, tetrahydrofuran, dichloromethane, acetonitrile... The complexes were characterized by a combination of analytical and spectroscopic techniques, including IR, UV–Vis, CHN elemental analysis. IR spectra of the complexes are also useful, as explained for the ligands. ^1H and ^{13}C NMR spectra of the complexes were not very informative as a result of the presence of paramagnetic Cu(II) atom (d^9).

3.3. Structure of [Cu(PhNCSPz)$_2$], 4

Single crystals suitable for an X-ray diffraction study of $[Cu(PhNCSPz)_2]$ were obtained by slow evaporation of a concentrated THF (or acetone) solution of the title compound at room temperature. An ORTEP diagram of **4** is presented in Fig. 2 and a selection of bond lengths and angles is given in Table 2. In the solid state, the structure of the title compound consists of monomeric *trans*-CuN_2S_2 units and the geometry around Cu atom is a four-coordinate perfect square planar with bond angles of 85.8°, 94.2° and 180° for S1–Cu–N1, S1–Cu–N1^i, and S1–Cu–S1^i (or N1–Cu–N1^i), respectively. The molecular geometry, bond angles and Cu–N distances(1.954 Å) in **4** are comparable to those of $[Cu(H_2B(3,5\text{-}Me_2Pz)_2)_2]$ [17] or $[Cu(H_2B(3,5\text{-}(CF_3)_2\text{-}Pz)_2)_2]$ [24]. Both of the Cu–S (2.281 Å) distances in **4** are equal and are similar to those found for $(NEt_4)_2[Bp'CuMoS_4Cu_2(\mu\text{-}Bp')_2Cu_2MoS_4CuBp']$ [17] or $(NEt_4)_2[MS_4(CuBp')_2]$ (M = Mo, W; $Bp' = H_2B(3,5\text{-}Me_2Pz)_2$) [18]. The structure of **4** is also very similar to that of the anionic *cis*-CuN_2S_2 complex, $[Cu(SCH_2CH(CO_2Me)NHCH_2)_2]^-$, which has been introduced as a synthetic model for the copper proteins such as poplar plastocyanin [25]. Even if, the bonding parameters about Cu atom in **4** are somewhat different from those of the mentioned metalloproteins, they match better than the previously reported complexes [25–28].

Table 2
Selected bond lengths (Å) and angles (°) for (**1**)

Cu1–S1	2.281(1)	Cu1–N1	1.954(2)
S1–Cu–S1^i	180	N1–Cu–N1^i	180
S1–Cu–N1	85.8(1)	S1–Cu–N1^i	94.2(1)

Symmetry code (*i*): $1-x, 1-y, 1-z$.

The structure of the complex **5** has also been determined, and the copper atom has a distorted tetrahedral geometry with bond angles varying from 86.93° to 151.59° and average Cu–N and Cu–S distances of 1.976 and 2.237 Å, respectively; The complete data for this structure will be published elsewhere as necessitated by our joint collaborators.

3.4. Conclusion

The compounds **1**–**3** are new anionic bidentate ligands which can be easily prepared and stored for months in dry air without any significant decomposition, according to their physical properties and IR spectroscopy. So, there is a vast possibility to do more research on these ligands by synthesizing new similar ligands via displacing the pyrazolyl moiety of the ligands with different similar pyrazole-type nucleophiles. Hence, coordination chemistry of the ligands will be structurally as well as functionally fruitful and interesting.

As a result of structural similarity, the complexes **4**–**6**, can be considered as structural models for type I mononuclear Cu-proteins such as poplar plastocyanin, cuperedoxin, cytochrome *c* oxides, etc. [20,26,29,30]. In addition to comparability of pyrazole (as N-donor in **4**–**6**) and imidazole of amino acids of living systems, the bonding parameters and co-ordination environment of Cu atom in **4** are similar to those reported for copper proteins. It is also fascinating that, according to our knowledge, the compounds **4**–**6** are among the rare complexes which contain stable Cu(II)–S (from thiolates)

bonds. The high stability of these complexes may arise from the tendency of Cu(II) to form square planar geometry, high ligand field stabilization energy, and the formation of two five-membered chelate rings.

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Appendix A. Supplementary data

Crystallographic data, excluding structure factors, have been deposited at Cambridge Crystallographic Data Center, CCDC No. 250916. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.01.019.

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